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1-alkyl-3-methylimidazolium Bis(pentafluoroethylsulfonyl)imide Based Ionic Liquids: A Study of Their Physical and Electrochemical Properties

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1-ALKYL-3-METHYLIMIDAZOLIUM BIS(PENTAFLUOROETHYLSULFONYL)IMIDE BASED IONIC LIQUIDS: A STUDY OF THEIR PHYSICAL AND ELECTROCHEMICAL PROPERTIES

A thesis submitted in partial fulfillment
of the requirements of the degree of
Master of Science

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jennifer Nicole DeCerbo ENTITLED 1-Alkyl-3-Methylimidazolium bis(pentafluoroethylsulfonyl)imide Based Ionic Liquids: A Study of Their Physical and Electrochemical Properties BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

DeCerbo, Jennifer Nicole. M.S., Department of Chemistry, Wright State University, 2008. 1-Alkyl-3-Methylimidazolium bis(pentafluoroethylsulfonyl)imide Based Ionic Liquids: A Study of Their Physical and Electrochemical Properties.

Ionic liquids are an attractive possibility for battery electrolytes. Five ionic liquids were synthesized using a 1-alkyl-3-methylimidazolium (XMI^+) cation, where the alkyl group was ethyl, propyl, butyl, pentyl, or hexyl, and a bis(pentafluoroethyl-sulfonyl)imide ($Beti^-$) anion. The absorption and desorption of water, conductivities, densities, viscosities, decomposition temperatures, and electrochemical properties were studied. These ionic liquids were found to absorb less water than previously studied ionic liquids with tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) anions. Their conductivities decreased with longer alkyl chains on the imidazolium cation and were lower than ionic liquids with BF_4^- as the anion. The densities of the ionic liquids decreased with increasing temperature and alkyl chain length. Viscosities decreased with increasing temperature but increased with increasing chain length. All of the ionic liquids were found to be thermally stable to nearly 400 ^oC. The potential windows increased with increasing chain length, from 4.2 V (EMIBeti) to 4.7 V (HMIBeti).

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DEDICATION

To my Mom, you have taught me more than you know. I am forever grateful for everything that you have given me. Thank you for always encouraging my ever changing "dynamic life plan."

To my Grandparents and Family, you have always been there for me. Your thoughts and memories are always with me. Thank you for your support and encouragement even if you don't know what I'm talking about a lot of the time!

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I. INTRODUCTION

Molten Salts and Ionic Liquids

Molten salts were first discovered over 200 years ago. A molten salt is a liquid that is entirely composed of ions and typically has a very high melting point. First used in the 19th century, molten salts were to verify the Laws of Electrolysis by Faraday and Davy and later in the isolation of alkali metals from molten alkali hydroxides.[1, 2] Some of the characteristics of molten salts which make them attractive candidates for use as battery electrolytes are their high thermal stability and electrolytic conductivity, high thermal capacity, low vapor pressure, low dielectric constant, low density, and wide range of thermochemical and electrochemical stability. Their main disadvantages are their corrosive and hygroscopic nature as well as their high operating temperature.

Some examples of molten salts are lithium chloride (LiCl) and potassium chloride (KCl) which have melting points of 610 ^{o}C and 776 ^{o}C, respectively.[3] At these temperatures, the electrochemical properties of these two salts have been investigated for their use in lithium batteries because they are conductive and chemically inert. However, the major drawback of these salts for use in lithium batteries is their corrosive nature, high viscosity, and high operating temperature.[4] In order to try to combat the high temperature constraints, researchers started to mix several salts to produce mixtures with lower melting points. One such example of this is a LiCl-KCl melt which has a melting point of 355 ^{o}C. Melts such as these are used in lithium, lithium sulfur, and lithium-alloy

sulfide batteries.[5] While these melts provide a lower melting temperature, an even lower melting electrolyte was needed for use in a battery.

In order to achieve the goal of a lower melting point molten salt, researchers turned their attention to the possibility of using more complex organic ions to make their molten salts. This led to the discovery of the first room temperature molten salt in 1914, which was composed of an ethylammonium cation and nitrate anion and had a melting point of 12 ^{o}C.[6, 7] Today, this type of low melting (below 100 ^{o}C) molten salt is called an ionic liquid. The chemical and physical properties of ionic liquids are interesting for several reasons, such as their high thermal stability, high conductivity, low density, extremely low vapor pressure, large electrochemical window, and their non-aqueous and non-toxic nature. These properties make them ideal for many applications including their use as reusable solvents in organic reactions, and as electrolytes in batteries and fuel cells. [7-13] The first class of ionic liquids to be studied extensively for these properties were the haloaluminate ionic liquids.

Haloaluminate Ionic Liquids

The first haloaluminate ionic liquids were synthesized at the United States Air Force Academy by Lowell A. King in the early 1950's. He was the first to use inorganic chloroaluminates in lieu of typical LiCl-KCl melts.[14] This allowed for decrease in the operational temperature of the system as well as decrease the degradation processes typically caused by molten salts. One example of this type of ionic liquid is a NaCl-$AlCl_3$ mixture which has a melting point as low as 107 ^{o}C, depending on the mole fraction. This new ionic liquid was useful in that it had a much lower melting point, but it was only useful as an electrolyte when the $AlCl_3$ concentration was at a mole fraction

of 0.66.[6] At this mole fraction, this compound was not a liquid below 175 ^{o}C which was higher than desired. It was also difficult to work with and characterize due to the molecular composition of Al_2Cl_6 which was present in the liquid and vapor states.

In the late 1940's, the scientists at the Rice Institute made the first low temperature organic chloroaluminate ionic liquid. It was composed of an alkylpyridinium halide and $AlCl_3$ and used in electroplating baths for aluminum.[15] The use of more organic based ionic liquids appeared to be a better route to pursue. In 1968, the researchers at the US Air Force Academy started investigating a 1:2 ratio of ethylpyridinium bromide (EPB) and $AlCl_3$ for use as an electrolyte for ambient temperature batteries. They expanded their work to include longer alkyl groups to produce new ionic liquids and found that butylpyridinium chloride-$AlCl_3$ (BPC-$AlCl_3$) had the highest conductivity of all of the compounds tested. Unfortunately, the major downfall was that its melting point was at 40 ^{o}C, just slightly over ambient temperature.[16]

In the late seventies to early eighties Charles L. Hussey and John S. Wilkes discovered a direct route to synthesizing 1-ethyl-3-methylimidazolium chloride-trichloroaluminate (EMICl-$AlCl_3$).[17, 18] The use of the imidazolium based ionic liquid was a great technological breakthrough because it had a liquid range of -100 ^{o}C to 200 ^{o}C depending on the mole ratio of EMICl to $AlCl_3$. This new ionic liquid had an electrochemical window 0.9 V larger than previous ionic liquids and was thermally stable and highly conductive. Its major disadvantages were the fact that impurities could greatly decrease its potential window and it was very air and moisture sensitive. Its sensitivity to moisture increased its corrosive nature by reacting with the water to produce HCl. In the past twenty years, dialkylammonium based ionic liquids have

become a highly investigated topic as they seemed to be a step in the right direction for creating an electrolyte with a more negative reduction potential than Al(III).[19]

Non-Chloroaluminate Room Temperature Ionic Liquids

In 1992, J. Wilkes and M. Zaworotko reacted 1-ethyl-3-methylimidazolium ion (EMI^+) with several different fluorinated anions to create a new type of ionic liquids.[20-22] The anions were tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and hexafluoro-arsenate (AsF_6^-). These ionic liquids were found to have lower reactivity with air and moisture than other ionic liquids. $EMIBF_4$ was found to have an electrochemical window of 4 V, higher than any previous ionic liquid.[20] Also, it was found to be thermally stable up to 300 ^oC.

In 1996, Grätzel, Bônhote, and coworkers published their work which used fluorinated organic anions in conjunction with 1,3-dialkylimidazolium cations.[23] Some examples of these anions are trifluoromethane (CF_3^-), and bis(perfluoromethylsulfonyl)-imide (NTf_2^-). They reported that these new fluorinated organic anions were not nearly as sensitive to moisture as BF_4^- and PF_6^- which made them good candidates for battery electrolytes since the anion would not undergo hydrolysis.

The development of these new ionic liquids opened the door to much more ionic liquid research. Scientists realized that they could not only alter the anion, but they could also alter the alkyl chain lengths on the cation, opening up the door to the possibility of thousands of new ionic liquids. The ability to control which cations and anions were used gave way to the ability to vary properties of the ionic liquid as desired. Some of the more commonly studied cations and anions are shown in Figure 1.

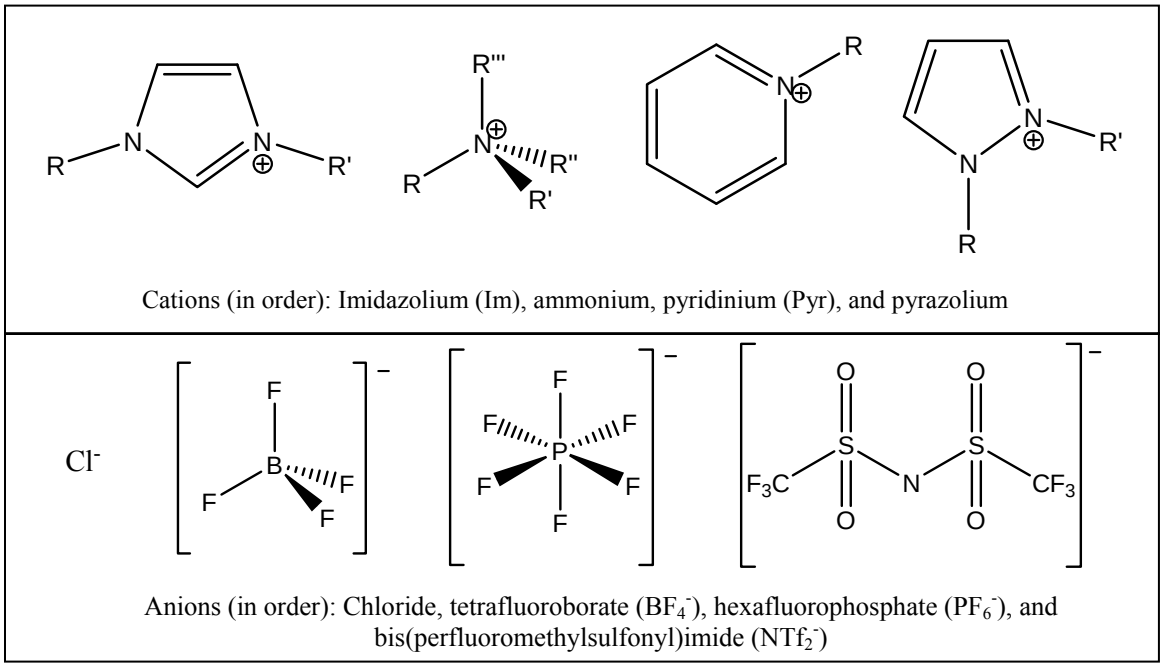


Figure 1. Common cations and anions used in the formation of ionic liquids.

Ionic Liquids as Green Solvents

In a world quickly becoming "green," ionic liquids are the perfect addition. Ionic liquids can be considered a "green solvent" as they have negligible vapor pressure and therefore do not pollute the environment. They can be substituted for traditional solvents in many organic reactions. In addition, many ionic liquids are non-flammable and are easily reusable.[6, 8, 10, 12, 24] The pairing of different cations with different anions allows for the synthesis of "designer solvents" whose properties can be tailored to the application of the ionic liquid.[7] For example, a more hydrophobic ionic liquid can be obtained by adding tetrabutylammonium (Bu_4N^+) to bis(perfluoromethylsulfonyl)imide (NTf_2^-) or a less hydrophobic ionic liquid could be created by using a short chain imidazolium cation and a chloride anion.[19] Other properties can be controlled via careful ion selection including density, viscosity, liquid range, and polarity.

It has already been shown that these systems can be used in organic separations[25], Diels-Alder,[26] hydrogenation,[6, 27, 28] Friedel-Crafts,[29, 30] and Grignard[31] reactions, and also as electrolytes in batteries.[8, 33-35]

Separations

Ionic liquids can be useful tools in many types of organic separations because they can simultaneously dissolve organics and inorganic species and are miscible with many substances that have a wide range of polarities.[7] Ionic liquids also have the advantage that they can be reused in separations. These properties allow for numerous opportunities to modify existing separation techniques and also open the door to the possibility of being able to separate new mixtures which could previously not be separated due to miscibility or limited liquid range constraints.

Diels-Alder Reactions

Ionic liquids are finding applications as solvents in well known organic reactions such as the Diels-Alder reaction. When ionic liquids are used as a solvent they greatly enhance the rate of the reaction. When coupled with a mild Lewis acid such as zinc(II) oxide, selectivities can be improved to 20:1 as compared to 4:1 when performed in an organic solvent.[26] For example, the ionic liquid $BMIPF_6$ has been used in a Diels-Alder reaction of isoprene and but-3-en-2-one as seen in Figure 2.

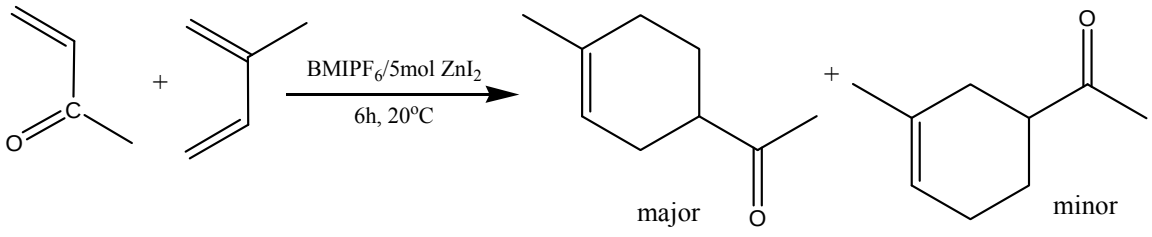


Figure 2. The reaction of isoprene and but-3-en-2-one catalyzed by ZnI_2 using $BMIPF_6$ as the solvent.

Another advantage of using ionic liquids as solvents includes their ability to be reused once the product has been recovered from the reaction. Also, the use of hydrophobic ionic liquids can allow more water sensitive reagents to be reacted where this would be more difficult in a traditional organic solvent. Other advantages of using ionic liquids for Diels-Alder reactions include their ability to be used over a wide temperature range (-40 ^{o}C – 200 ^{o}C) and under pressure, as well as their non-oxidizing and non-explosive nature.[26]

Hydrogenation Reactions

In a typical hydrogenation reaction, a carbon-carbon double bond is broken using a transition metal complex as a catalyst dissolved in an organic solvent. Recently, studies have been performed that use transition metal complexes dissolved in ionic liquids to perform these same reactions, obtaining comparable yields without generating the waste associated with a typical organic solvent. Suarez et al. have reported using Ru(II) and Co(II) complexes dissolved in $BMIBF_4$ to catalyze the reaction of butadiene into but-1-ene with selectivities of up to 100% depending on the conditions of the reaction.[27] Chauvin and Olivier-Bourbigou report considerably higher turnover frequencies in the hydrogenation of 1-pentene to pentane using a Ru(III) based catalyst in $BMIBF_4$ or $BMIPF_6$ as compared to the traditional solvent of acetone.[28] Studies have also reported a higher conversion rate and higher turnover rates for the conversion of 1-cyclohexene to cyclohexane using rhodium based catalysts in $BMIBF_4$.[6] These are important discoveries as they could lead to the use of ionic liquids in industrial applications instead of volatile organic solvents.

Friedel-Crafts Reactions

Friedel-Crafts reactions are a set of reactions developed by Charles Friedel and James Crafts in the late 1870's.[35] The two main reactions are the alkylation of an aromatic ring and the acylation of an aromatic ring. In a typical Friedel-Crafts alkylation reaction, an aromatic ring is reacted with an alkyl halide using a strong Lewis acid catalyst such as $FeCl_3$. In an acylation reaction, an aromatic ring is acylated in the presence of a strong Lewis acid catalyst. These reactions typically take place under anhydrous conditions over the course of several hours. Holbrey and Seddon report the successful alkylation and acylation of aromatic rings using chloroaluminate (III) ionic liquids, which acted as the solvent and the catalyst in these reactions.[29] In 1998, Stark et al. reported the ability to use an N-ethyl-N'-methylimidazolium iodide/halogenaluminate ionic liquid as the catalyst and solvent in the acylation of ferrocene as seen in Figure 3.[30]

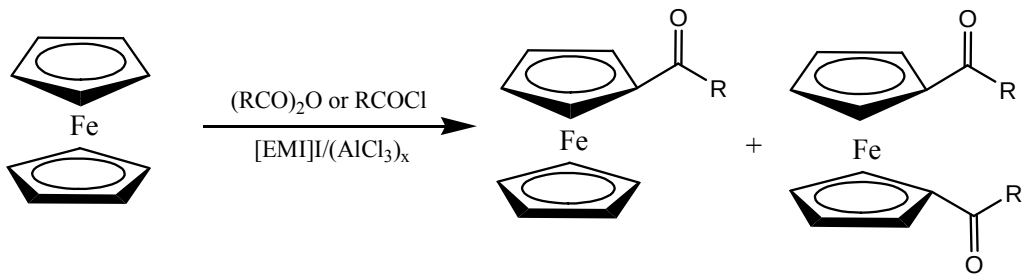


Figure 3. The acylation of ferrocene using an N-ethyl-N'-methylimidazolium iodide/halogenaluminate ionic liquid as both the solvent and the catalyst.

Grignard Reactions

Grignard reactions are commonly used in organic chemistry to produce alcohols. Handy recently reported the successful reduction of an aldehyde to an alcohol via a Grignard reagent as seen in Figure 4.[31]

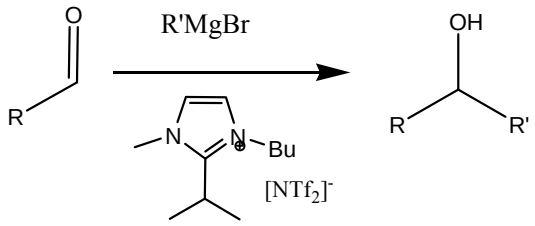


Figure 4. Use of a novel ionic liquid as a reusable solvent in a Grignard reaction.

He was able to synthesize the new ionic liquid as well as achieve yields near 60% in the reaction, which is a reasonable result. In addition, the ionic liquid was found to be easily reusable for several reactions without obvious hindrance of the reaction.

Electrolytes for Batteries

The wide electrochemical window, high thermal stability, wide liquid range, high conductivity and lack of vapor pressure make ionic liquids good candidates for battery electrolytes.[32] A good battery has an electrolyte that will not oxidize or reduce over the electrochemical window in which it is intended for use. For example, in a lithium ion battery, a lithium atom (Li^o) is oxidized to a lithium ion (Li^+) at the anode and is then reduced back to Li^o at the cathode. If the electrochemical window of the electrolyte is not large enough to allow this transition, the Li^+ will react with the electrolyte, rendering the battery ineffective. Many types of batteries also run at elevated temperatures (higher than room temperature) so having an electrolyte that will not evaporate or degrade is also a very important factor. In addition, a highly conductive electrolyte is necessary in order to promote Li^+ movement through the electrolyte from the anode to the cathode in order to produce electricity. An electrolyte with a wide liquid range also allows for the solvation of a wide variety of inorganic, organic, and organometallic species which is very useful for battery applicaions.[19]

Ionic liquids such as 1,2-dimethyl-4-fluoropyrazolium tetrafluoroborate ($DMFBF_4$) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) are being investigated for their use in batteries as they have wide electrochemical windows, much greater than that of aqueous electrolytes.[33] Pyrazolium based ionic liquids are very promising for use as an electrolyte in lithium batteries because they do not react with the lithium metal at higher temperatures.[14] Another reason ionic liquids are such good candidates for battery electrolytes is due to the fact that many of them are resistant to water absorption which helps sustain the life and efficiency of the battery.[34]

Synthesis of 1-alkyl-3-methylimidazolium Based Ionic Liquids

The first step in synthesizing an ionic liquid is to use a quaternization reaction of an alkyl halide, typically Cl^-, and N-methylimidazole (Figure 5). This reaction is typically performed in an inert atmosphere to prevent contamination by O_2 and water. Clear halide salt crystals are formed.

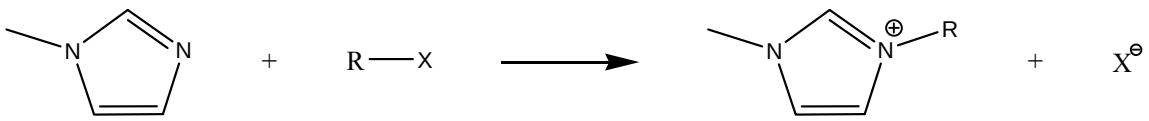


Figure 5. The quaternization reaction of N-methylimidazole and an alkyl halide to produce a halide salt. For the products, R can be an ethyl (EMI^+), propyl (PMI^+), butyl (BMI^+), pentyl ($PnMI^+$), or hexyl (HMI^+) group.

An anion exchange is then performed on the halide salt, exchanging the halide for another negatively charged ion resulting in the formation of an ionic liquid (Figure 6).

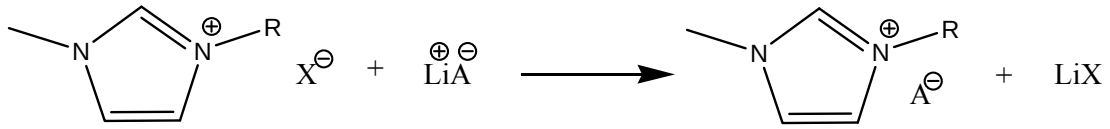


Figure 6. The anion exchange reaction resulting in an ionic liquid.

The purification of ionic liquids is a very important aspect of their synthesis. Impurities in the ionic liquid can have negative impacts on the electrochemical potential window, thermal properties, density, and viscosity of the ionic liquid.[19] Discoloration is an obvious sign of contamination as most ionic liquids should be clear. To help prevent discoloration, the glassware used in synthesizing the ionic liquid should not be washed with acetone, as acetone has been found to cause a yellow color in the ionic liquid.[19] Also, the N-methylimidazole is typically redistilled prior to use to remove any contaminants. The presence of oxygen during the initial quaternization reaction can lead to discoloration and water can also interfere with this reaction, causing side reactions.[19] Once halide salt crystals have formed, they are often recrystallized with acetonitrile and ethyl ether to remove any remaining impurities.

Once the anion exchange reaction has occurred, the ionic liquid is typically washed several times with deionized water to remove any residual traces of the halide. Vacuum filtration can also be used to filter out unwanted salts produced in the anion exchange reaction. In extreme cases, titration with $AgBF_4$ can be performed to remove trace amounts of chloride left in the ionic liquid. Following the removal of unwanted ions, the ionic liquid should be dried in a vacuum to remove any traces of water. Water has been shown to reduce the electrochemical potential window by several volts when undergoing reduction and oxidation within the potential window of the ionic liquid.[19] Water can also react with components of the ionic liquid, particularly the anion, to further

reduce the electrochemical window or even cause the ionic liquid to become corrosive due to the formation of HF.[19]

Properties of 1-alkyl-3-methylimidazolium Based Ionic Liquids

Thermal properties

The thermal properties, such as decomposition temperature, melting point, and glass transition temperature (T_g), of many ionic liquids have been studied. Thermal gravimetric analysis (TGA) is used to determine the decomposition temperature of materials. Most 1-alkyl-3-methylimidazolium based ionic liquids have a decomposition temperature above 350 ^oC[19] and often above 400 ^oC.[8, 32, 36, 37] A few of the most common 1-alkyl-3-methylimidazolium based ionic liquids' decomposition temperatures are listed in Table 1.

Table 1. The decomposition temperatures of some of the more common 1-alkyl-3-methylimidazolium based ionic liquids.

Ionic Liquid	Decomposition Temperature (^oC)	Reference
$MMINTf_2$	444	36
$EMIPF_6$	375	32
$EMINTf_2$	439, 455	36, 32
$PMIPF_6$	335	32
$PMINTf_2$	452	32
$BMIBF_4$	361, 425	8, 37
$BMIPF_6$	433	37
$BMINTf_2$	427, 422	36, 8
BMIBeti	402	37
$HMINTf_2$	428	36
$C8MINTf_2$	425	36

It has been determined that using large, asymmetric ions in the synthesis of ionic liquids leads to a lower melting point ionic liquid due to charge delocalization which

disrupts the packing efficiency of the ionic liquid.[19] In imidazolium based ionic liquids, the coulombic charges present in the ions are disrupted, leading to lower melting points than ionic liquids based on other cations. It has been shown that the alkyl groups on the imidazolium do not have a large effect on the melting point of an ionic liquid as their influence is not nearly as strong as the coulombic interactions between the cation and anion.[19] However, when comparing differing alkyl chains for ionic liquids with the same anion, the melting point tends to decrease with increasing chain length.[38]

Imidazolium based ionic liquids have a fairly small range of glass transition values. They typically range from -76 to -92 ^{o}C.[8, 32, 36, 39] It has been observed that many ionic liquids undergo a supercooling effect in which their melting and freezing points differ by as much as 84 ^{o}C.[37] This can make the determination of the melting and freezing points increasingly difficult due to instrument constraints.

Density and Viscosity

The density of most 1-alkyl-3-methylimidazolium based ionic liquids ranges from 1.0 – 1.6 g/mL.[10] When comparing the density of ionic liquids with differing anions, the density is typically related to the molar mass of the ionic liquid; ionic liquids with heavier atoms tend to be more dense than those with smaller atoms.[10] $EMIBF_4$ ionic liquids have densities near 1.2 g/mL while $EMINTf_2$ ionic liquids have densities near 1.5 g/mL (Table 2). As the alkyl chain length increases on the cation, the density decreases in a fairly systematic manner.[7, 10, 19] The density has also been shown to decrease linearly with increasing temperature. Jacquemin et al. studied the density of dry and water saturated ionic liquids of different cation chain lengths and found the density of both the dry and water saturated ionic liquids decreased in a linear fashion with increasing temperature.[10]

Table 2. The densities of some common ionic liquids at 25 °C.*

Ionic Liquid	Density (g/mL)	References
$EMIBF_4$	1.279, 1.24	37, 40
$PMIBF_4$	1.21	40
$BMIBF_4$	1.2, 1.7(20)	41, 42
$BMIPF_6$	1.37, 1.36	41, 42
$MMINTf_2$	1.559(22), 1.57	10, 41
$EMINTf_2$	1.52(22), 1.51, 1.518	23, 41, 37
$BMINTf_2$	1.43, 1.429(19), 1.37	41, 23, 41
$HMINTf_2$	1.31	41

*Temperatures noted in parenthesis if different than 25 °C.

The viscosity of 1-alkyl-3-methylimidazolium ionic liquids typically ranges from 10 – 500 mPa·s at ambient temperature which is two to three times greater than the viscosities of traditional organic solvents such as methanol or toluene.[10] The viscosity is governed by van der Waals interactions and hydrogen bonding between the cations and anions. Typically, an increase in viscosity is observed with longer alkyl chains due to increased van der Waals interactions between the cations.[19, 23] Examples of this can be seen in Table 3. One interesting characteristic of the bistrifyl based anions (NTf_2^-) and $Beti^-$ (bis(pentafluoroethylsulfonyl)imide)) is that they have viscosities nearly an order of magnitude less than their PF_6 relatives. The viscosity has also been shown to greatly decrease with increasing temperature which is typical of many liquids.[10, 36] The high density of the ionic liquids can be a disadvantage for some applications. When its use is considered for battery applications, the viscosity is a major disadvantage because it reduces its ability to efficiently perform mass transfer as an electrolyte in a cell.[7] This problem can be mediated due to the fact that many batteries run at elevated temperatures which could help reduce the viscosity.

Table 3. The viscosities of some common 1-alkyl-3-methylimidazolium based ionic liquids at 25 °C.*

Ionic Liquid	Viscosity (mPa·s)	References
$EMIBF_4$	32, 37	37, 40
$BMIBF_4$	75	41
$BMIPF_6$	182	41
$MMINTf_2$	44, 31	23, 41
$EMINTf_2$	34(20), 28, 27	23, 43, 41
$PMINTf_2$	60	35
$BMINTf_2$	40, 52(20), 56	41, 23, 41
$HMINTf_2$	71	41
EMIBeti	61(26)	44
BMIBeti	87	41

*Temperatures noted in parenthesis if different than 25 °C.

Solvent Miscibility

The absorption of water by ionic liquids is a great obstacle that has been studied in detail. All ionic liquids absorb water to some extent; the immensity of that extent depends on the composition of the ionic liquids. Cammarata et al. performed a study of 1-alkyl-3-methylimidazolium cations paired with PF_6^-, BF_4^-, and NTf_2^- anions to study the molecular states of water molecules absorbed by the ionic liquid.[45] They found that hydrogen bonding occurs with each of the anions in a 1:2 type hydrogen bonding complex such that one water molecule is hydrogen bonded on either side to the anion. Their study also showed that PF_6^- has the weakest and NTf_2^- has the strongest hydrogen bonding capabilities of the three anions.

The ability of gases to dissolve in ionic liquids has also been investigated. This is important because ionic liquids are used in hydrogenation, hydroformylation, and oxidation reactions which can involve reactants in the gas phase.[46] Also, understanding how compressed gases and supercritical fluids dissolve in ionic liquids is important for assessing the feasibility of using ionic liquids for certain applications. In addition,

important information regarding the solvent behavior of the ionic liquids can be extracted from studying the interactions of gases and the ionic liquids.[46]

The solubility of 1-alkyl-3-methylimidazolium based ionic liquids in organic solvents has also been investigated.[47] It is imperative to know how these phases interact with one another in order to determine their usefulness as solvents in organic reactions. Also, it is important to know which ionic liquids are soluble in organic solvents in the event that the product of a reaction needed to be extracted from the ionic liquid. Information regarding the polarity of an ionic liquid can also be investigated by dissolving them in organic solvents.[48]

Electrochemical Properties

The electrochemical properties of 1-alkyl-3-methylimidazolium ionic liquids are a key aspect for their application to batteries and other power sources. Ionic liquids tend to have large electrochemical windows in comparison to other solvents (Table 4).

Table 4. The electrochemical potential window of some common ionic liquids.

Ionic Liquid	Potential Window (V)	Working Electrode	Reference Electrode	References
$EMIBF_4$	4.3, 4.5	Pt, Pt	Ag|AgCl - wire	49, 50
$BMIBF_4$	4.2, 4.1	GC, Pt	$Li\|Li^+$	40, 51
$BMIPF_6$	4.4, 4.2	Pt, CNT	$Ag\|Ag^+$ in DMSO	52, 53
$EMINTf_2$	4.3, 4.1, 4.5	Pt, Pt, GC	$I^-\|I_3^-$, Ag wire	23, 44, 54
$PMINTf_2$	4.3	GC	$Li\|Li^+$	40
$BMINTf_2$	4.6	Pt	$Ag\|Ag^+$ in DMSO	52
EMIBeti	4.1	GC	Ag wire	44

The electrochemical window of an ionic liquid depends primarily on the resistance of the anion to oxidation and the cation to reduction.[19] Studies have determined the stability of the anion towards oxidation to be Cl^-, F^-, Br^- (halides) <

$[AlCl_4]^-$ (chloroaluminates) $\leq$ PF_6^-, AsF_6^- (fluorinated ions) $\leq$ NTf_2^-, $(C_2F_5SO_2)N^-$ (trifyl ions) ~ BF_4^-.[19] In addition, studies have determined the stability of the cation towards reduction to be pyridinium < imidazolium $\leq$ pyrazolium $\leq$ ammonium for the cations mentioned previously.

The conductivity is another important electrochemical property of ionic liquids for use as battery electrolytes. Conductivity is a measure of the available charge carriers and their mobilities within a matrix.[19] A good electrolyte has a high conductivity so that it can easily transport ions across the electrolyte from one electrode to the other. Ionic liquids tend to have good conductivity and solvent transport properties which makes them ideal for electrolytes (Table 5).

Table 5. The conductivity values of some common ionic liquids at 25 ^oC (unless otherwise noted).

Ionic Liquid	Conductivity (mS/cm)	References
$EMIBF_4$	14, 13(26)	55, 44
$PMIBF_4$	5.9	40
$BMIBF_4$	3.5, 1.73(20)	40, 42
$EMIPF_6$	5.2	19
$BMIPF_6$	1.8(22), 1.4	55, 42
$MMINTf_2$	7.2	19
$EMINTf_2$	8.8(20), 9.2, 5.7	23, 42, 37
$BMINTf_2$	3.9(20)	23
EMIBeti	3.4(26)	44

In some cases, the conductivity can be smaller than expected. This can be attributed to a decrease in available charge carriers due to ion pairing or ion aggregation of the ionic liquid.[19] Another cause of smaller conductivity is attributed to reduced ion mobility due to the large ion sizes found in many ionic liquids. Conductivity has been shown to be correlated weakly with cation size and type such that increasing the cation size leads to a lower conductivity. This can be attributed to an increased ion size

decreasing the mobility of the ions. No clear relationship has been established between conductivity and the anion.[19]

Electrochemical Cells

One type of electrochemical cell, a galvanic cell, is a system that converts chemical energy from an oxidation-reduction reaction to electrical energy. They are more commonly referred to as batteries. There are three main parts: the anode, the cathode, and the electrolyte. Oxidation occurs at the anode, and the electrons that are released travel through an external circuit to the cathode, producing electricity (Figure 7). The ions produced during oxidation travel through the electrolyte to the cathode where reduction takes place.

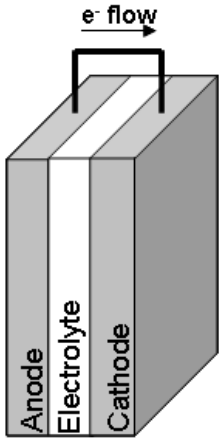


Figure 7. A typical battery cell where electrons are released from the anode and travel through an external circuit to the cathode.

The anode is typically made up of a metal that is easily oxidized and very conductive.[57] The cathode is usually composed of metal oxides because they are relatively easy to reduce. A good electrolyte is highly conductive and is typically an aqueous salt solution or paste.

The first battery was discovered by Alessandro Volta in 1800.[4] He described a stack of alternating disks composed of zinc and silver separated by pieces of paper soaked in a salt solution. The cell underwent the following reaction:

$$Zn + 2Ag^{+} \longrightarrow Zn^{2+} + 2Ag$$

The potential uses for this type of cell were quickly realized and by the 1830's these batteries were commercially available.[4] As the demand for batteries increased, a demand for better batteries arose. In 1866, Georges Leclanché developed the first dry cell battery.[5] Since then, the battery industry has flourished, providing the world with numerous types and sizes of batteries, all with different power capabilities.

There are two main types of batteries: the primary cell and the secondary cell. Primary cells are single use cells; once the chemicals are consumed in the discharge process, the cell can no longer be used and must be disposed of properly. A secondary battery is rechargeable. It uses a reversible redox reaction and can be charged and discharged several times before it loses its ability to be useful. In order to charge these types of batteries, a current is passed through the cell in the opposite direction of the discharge current.[57]

Primary Cells

The first primary cell was the Leclanché cell.[4] This cell uses a zinc anode and carbon-manganese dioxide cathode. The shorthand notation for this cell is as follows:

$$Zn(s) \mid Zn^{2+}(aq), NH_4^{+}(aq) \mid Mn_2O_3(s), MnO_2(s), C(s)$$

The overall reactions of the cell are:

$$\text{Anode: } Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$

$$\text{Cathode: } 2MnO_2(s) + 2NH_4^{+}(aq) + 2e^{-} \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

Some of the first cells used an aqueous electrolyte of ammonium chloride and zinc chloride but more modern cells use an electrolyte paste to help prevent leakage of the electrolyte during discharge.[5] Some other types of primary cells include zinc-mercuric oxide, metal-air, and lithium batteries. These cells are desirable due to the low production costs, long shelf life, and high energy density for low to moderate discharge rates. Their main disadvantage is that they must be disposed of after discharge and they often contain harmful components.

Secondary Cells

As previously mentioned, secondary cells are rechargeable batteries. The demand for this type of battery has become much greater as portable electrical technology, such as cell phones, laptops, and mp3 players, grows at an astonishing rate.[58] There is a great demand for a battery with a long life and a long life cycle; that is, a battery that lasts a long time before needing to be recharged and can also be recharged numerous times. Several types of batteries have been produced to try to meet these demands. It has suggested that the new electric cars will use batteries as opposed to fuel cells because they can reuse the same chemicals to convert chemical energy to electrical energy where fuel cells require a continuous flow of fuel. Below are more details regarding several types of rechargeable batteries.

Lead-Acid Batteries

The lead-acid cell was first designed by Gaston Planté in 1859.[4, 5] It is the most commonly used secondary cell today. The cell utilizes a lead dioxide cathode and a lead sponge anode which are both immersed in an electrolyte composed of sulfuric acid, summarized as follows.

$$Pb(s), PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s), PbO_2(s), Pb(s)$$

The net reaction is as follows:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(l)$$

The main use of this type of cell is for starting the engine in automobiles. These cells are fairly inexpensive to produce, have excellent reversibility of the electrochemical process, have a long life cycle, and they are able to operate over a wide range of temperatures. Their main disadvantages are the weight of the lead in the cell and its toxicity.[4]

Nickel-Cadmium Batteries

The first nickel-cadmium (Ni-Cd) battery was developed in 1899 by Waldemar Jungner.[4] These batteries have a nickel oxyhydroxide cathode and a cadmium anode. A schematic of the cell is as follows:

$$Cd(s), Cd(OH)_2(s) \mid KOH(aq) \mid Ni(OH)_2(s), NiO(OH)(s)$$

The following reactions occur within the cell:

$$\text{Cathode: } NiO(OH) + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^-$$

$$\text{Anode: } Cd + 2OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$$

These types of cells are easily recharged because the products formed in the reactions are insoluble hydroxides that will remain on the surface of the electrodes. Ni-Cd batteries are better at delivering high rates of power because they have very little internal resistance.[58] This makes them good for applications such as portable power tools. Ni-Cd batteries also have a constant discharge voltage, good performance at low temperatures, and can undergo hundreds of charge-discharge cycles. Some of the

disadvantages of Ni-Cd batteries are the toxicity associated with the cadmium, cost, and their inability to hold a charge when not in use. In addition, Ni-Cd batteries are affected by the "memory effect" where the battery life will shorten due to recharging when the battery has not been fully discharged.[4, 58]

Lithium and Lithium Ion Batteries

Lithium is a very attractive anode material due to its high standard reduction potential of 3.04 V at 25 ^{o}C, low density of 0.51 g/mL, and low electrochemical equivalent weight. This allows for cells to be made with higher energy densities, higher voltages, low self-discharge rates, and good charge retention.[5, 58] Lithium batteries require the use of a nonaqueous electrolyte due to the fact that lithium easily reduces water.[59] Lithium is currently being used in lithium batteries as well as lithium ion batteries which both use the electrolyte to transport lithium ions and countercharge ions between the cathode and anode.[58] Unlike other cells, the electrodes to not participate in the electrochemical reactions.

The first lithium batteries were made in 1962 by J. Chilton and G. Cook.[60] The positive electrode was made up of metallic halide salts such as AgCl, $CuCl_2$, or $NiCl_2$ while the negative electrode was composed of lithium metal. The electrolyte was a LiCl-$AlCl_3$ mixture dissolved in propylene carbonate, which led to the deterioration of the positive electrode by reacting to form soluble complexes such as $CuCl^{2-}$, which causes irreversible electrochemical reactions within the cell. This problem was remedied by the development of solid materials that could be used as electrolytes in the early 1970's.[61] These new solids were capable of hosting the lithium ions and the electrons without the concern of causing their own crystal lattice to destruct.

The first cathode material for the lithium battery was the highly conductive TiS_2. It was first marketed in a rechargeable lithium battery coupled with a LiAl negative electrode by Exxon and was used for watch batteries.[60] Other insertion materials that were considered for lithium batteries include $NiPS_3$,[62] MoS_2,[63] MnO_2, and V_2O_5.[64] In the early 1980's, Li_xCoO_2 and Li_xNiO_2 were proposed as possible positive electrode materials.[65] These two insertion materials, along with $LiMn_2O_4$[60] are currently being used as positive electrodes in the development of lithium batteries.[66]

The use of a lithium metal electrode is not without its faults. Lithium metal often becomes corroded during its life cycle, causing dendrites to form from the repeated charging and discharging of the cell.[4, 5, 59, 60] This causes a need for additional lithium metal to be added to the cell to compensate for the lithium lost due to dendrite formation.[4, 5] The dendrite formation is accelerated due to the lithium that is plated during recharging. That lithium is often porous, which increases the surface area of the electrode, causing an increase in the reactivity with the electrolyte. This further promotes dendrite formation which can lower the thermal stability of the cell and increase the cell's risk of short circuiting and catching fire.[5] The first attempts at combating dendrite formation used a lithium alloy (LiAl) but there were problems with volume changes and lithium diffusion.[4, 5]

Further advances in solving the problem with dendrite formation were made with the development of the lithium ion battery. This type of cell contains no lithium metal and lithium metal is not plated during the cell reactions. Lithium ion batteries use a carbon insertion material as the negative electrode which can incorporate up to six lithium atoms per carbon into its lattice structure.[5, 58] The lithium ions are intercalated

into the negative electrode during charging and released during discharge, as shown in Figure 8.[57]

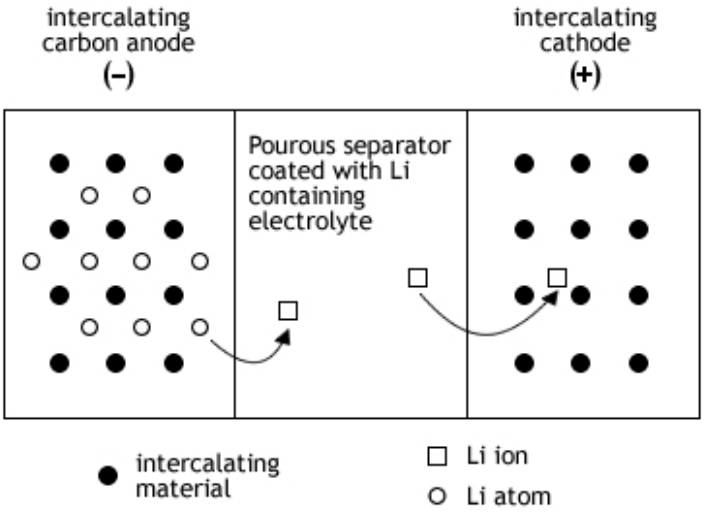


Figure 8. Lithium transport (discharge) in the lithium ion battery.

This is a reasonable substitution for lithium metal as the lithiated carbon battery has nearly the same voltage as the lithium metal battery.[5]

The electrolyte in a lithium ion battery is also very important. As previously mentioned, the electrolyte must be nonaqueous. It must also have a wide electrochemical potential window (0 – 5 V) because the electrolyte is constantly subjected to a dc bias that is equal to the cell voltage during assembly.[57] If the electrolyte is not stable towards this bias, is will degrade and render the cell useless. The electrolyte must also be conductive, thermally stable, and be compatible with the other components of the cell.

The most common electrolytes in lithium and lithium ion batteries are aprotic solvents, commonly cyclic esters such as propylene carbonate and ethylene carbonate, that contain inorganic salts such as $LiAsF_6$ or $LiBF_4$ to help increase conductivity.[66] The main disadvantage to using organic solvents is that they can explode or catch fire under stressful and abusive conditions, not unlike those inside of the cell.[4, 5, 66] This requires

that special safety devices be installed in each battery that will trigger the cell to shut down if it begins to overheat which adds to the production cost.

Ionic Liquids in Lithium and Lithium Ion Batteries

The first ionic liquid to be studied as a battery electrolyte was a melt containing aluminum chloride and 1-ethyl-3-methylimidazoium chloride.[56] This melt has conductivities ranging from 11.7 – 22.7 mS/cm and a potential window of about 3.6 V, depending on the ratio of the two components.[18] Lithium batteries have been tested using this type of electrolyte. They found that lithium deposition was reversible when $SOCl_2$ was added to the mixture, giving rise to the possibility of using the melt in batteries with rechargeable lithium anodes.[67] The major disadvantage of using this type of melt in a lithium battery is its tendency to react with moisture and form HCl which can erode the cell. This is one of the reasons why much more research has recently been focused on more air and moisture stable ionic liquids for use as battery electrolytes.

1,3-Dialkylimidazolium cations can be coupled with tetraflurorborate (BF_4^-) and trifluoromethansulfonate ($CF_3SO_3^-$) to decrease their air and moisture sensitivity while maintaining the electrochemical potential windows and conductivities necessary for a lithium ion battery electrolyte.[57] In addition, lithium ion test cells, called dual intercalating molten electrolyte (DIME) batteries, have been developed that use the EMI^+ cation coupled with one of the following anions: $AlCl_4$, BF_4^-, PF_6^-, or $CF_3SO_3^-$.[68] The DIME batteries, have electrodes composed of a graphite intercalating material, and a single ionic liquid as the electrolyte. These batteries are much safer and less toxic than many batteries due to the fact that no manganese, nickel, or cobalt oxides went in to the production as in most lithium ion batteries. Other studies have been done in which an

ionic liquid is mixed with one of the typical organic electrolyte solvents to see how they perform in the cells.[57]

II. EXPERIMENTAL

Materials

N-methylimidazole (99+%) was purchased from Aldrich Chemical Company, Inc. and purified prior to use by vacuum distillation at 65 ^{o}C and 100 mm Hg. 1-Chloro-ethane gas (99.7+%), 1-chloropropane (98%), 1-chlorobutane (anhydrous, 99.5%), 1-chloropentane (99%), and 1-chlorohexane (99%) were all purchased from Aldrich Chemical Company, Inc. and used as received. Lithium bis(pentafluoroethanesulfonyl)-imide (FC-130) was received from 3M Corporation and used without further purification. Silver tetrafluoroborate ($AgBF_4$) was purchased from Alfa Aesar Co. and used as received. Deuterated acetone and acetonitrile (99.5+%) were purchased from Sigma-Aldrich. The viscosity standard used to calibrate the viscometers was a Certified Viscosity Reference Standard, N100 (lot #08101) from Cannon Instrument Company.

Instrumentation and Characterization

Fourier-Transform Nuclear Magnetic Resonance Spectroscopy

Fourier-transform nuclear magnetic resonance (FT-NMR) spectra were obtained using a Bruker 300 MHz FT-IR. Both ^{1}H and ^{13}C DEPT-135 spectra were collected. The samples were run using deuterated acetone as the solvent. The spectra are shown in the Appendix.

Absorption and Desorption of Water

Water content in the ionic liquids was measured using a Denver Instruments Coulometric Karl Fischer Titrator, Model 260 which was calibrated using a Hydranala-Water Standard 1.00 (#34828, Riedel-de Haën). Samples ranging from 15-25 μL were injected into the titrator using a glass syringe with a stainless steel needle. The syringe was dried in an oven at 60-80 ^{o}C prior to use. To study the absorption of water by the ionic liquids at room temperature, a 2 mL sample was placed into a vial and put into a polymer glove box (Coy Laboratory Products). The humidity inside the glove box was set to 60% RH, controlled using an Electro Tech Systems (ETS) Automatic Humidity Controller (Model 514). The samples were exposed to the humid atmosphere for various amounts of time, removing a small amount (~60 - 100 μL) for each time interval to test for water content. The samples were not stirred during this process. Water desorption was studied in the same manner, reducing the humidity in the chamber to 6% RH and taking water content measurements at various intervals.

Fourier-Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectra were obtained using a Mattson Genesis II FT-IR spectrometer (model number 960M0000) operating from 400 to 4000 cm^{-1}. The spectra were analyzed using WinFirst Version 3.61 software. The liquid samples were pressed between two NaCl plates to acquire the spectra.

Density

The density of the ionic liquids was measured using a 1 or 2 mL volumetric flask. The flask was calibrated by measuring the density of water at 20, 30, 40 and 50 ^{o}C and comparing the values obtained to standard tables. To measure the density of the ionic

liquids, the ionic liquid was placed into the flask up to the mark, sealed, and placed into a temperature bath for ten minutes to allow the temperature to equilibrate. The flask was then removed from the bath, dried, and weighed immediately. Each sample was measured at least three times to determine an average value.

Viscosity

Viscosity measurements were taken at 20 ^{o}C and 30 ^{o}C using a Cannon 415 A817 Cannon-Fenske Routine glass viscometer manufactured by Cannon Instrument Company (Figure 9). The viscometer was calibrated using a Certified Viscosity Reference Standard, N100 (lot #08101) from Cannon Instrument Company (Table 6). The viscometer constant was determined to be 2.564 mm^2/sec^2.

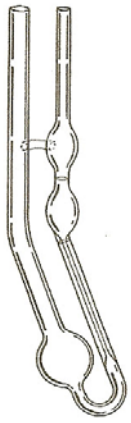


Figure 9. A Cannon-Fenske viscometer used for measuring viscosity.

Table 6. The calibration data for the Cannon 415 A817 Cannon-Fenske Routine glass viscometer measured at 20 ^{o}C.

Time (s)	Kinematic Viscosity (mm^2/s)	Viscometer Constant (mm^2/s^2)
127.9	323.1	2.526
124.4	323.1	2.597
125.7	323.1	2.570
126.1	323.1	2.562
Average		2.564 $\pm$ 0.0029

For measuring the viscosity at 40 and 50 ^{o}C, a 300 Cannon-Fenske Routine glass viscometer with a viscometer constant of 0.3891 mm^2/sec^2 was used (Table 7).

Table 7. The calibration data for the Cannon 300 Cannon-Fenske Routine glass viscometer measured at 50 ^{o}C.

Time (s)	Kinematic Viscosity (mm^2/s)	Viscometer Constant (mm^2/s^2)
151.12	59.73	0.3952
153.00	59.73	0.3904
155.00	59.73	0.3854
154.97	59.73	0.3854
Average		0.3891 $\pm$ 0.0047

In order to measure the kinematic viscosity, the sample was brought to a constant temperature in a water/isopropanol bath. After 10 minutes, the sample was removed from the bath and the time it took for the ionic liquid to flow through the viscometer was measured immediately, performing at least three measurements. For higher temperatures, the viscometer was kept in the water bath as much as possible to ensure the ionic liquid was kept at a constant temperature. The time was then multiplied by the viscometer constant to get the kinematic viscosity. For example:

$$25.78 \text{ s} \times 2.564 \text{ mm}^2/\text{s}^2 = 66.10 \text{ mm}^2/\text{s}.$$

Absolute viscosity, η, was determined by multiplying the kinematic viscosity by the density of the sample as shown below.

$$66.10 \text{ mm}^2/\text{s} \times 1.597 \text{ g/mL} = 105.6 \text{ mPa}\cdot\text{s}.$$

Thermal Gravimetric Analysis

Thermal gravimetric analysis was performed using a Perkin Elmer 7 Series Thermal Analysis System operating under nitrogen. The temperature scan ranged from 30 ^{o}C to 500 ^{o}C with a heating rate of 10.0 ^{o}C min^{-1}. Each sample size was

approximately 7-10 mg. The system was cleaned prior to each sample to remove any remaining salt traces.

Conductivity

Conductivity data were obtained using an Oakton Conductivity Meter, model WD-35607-10, and a modified glass MI-915 conductivity electrode manufactured by Microelectrodes, Inc. The sample size was approximately 0.5 - 1 mL (Figure 10).

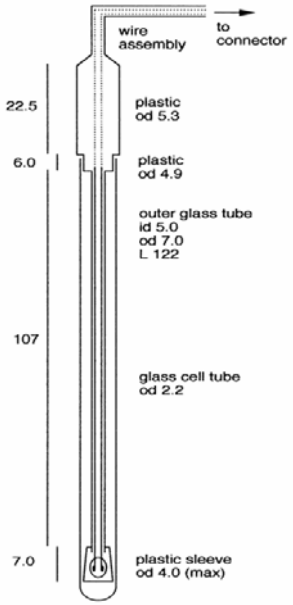


Figure 10. The setup for the conductivity measurements.

The cell constant of the electrode was determined by measuring the conductance of several standard solutions of potassium chloride with concentrations ranging from 0.1 M to 0.01 M at room temperature. The cell constant was found by plotting the specific conductance, κ (mS/cm), against the measured conductivity, L (mS), (Figure 11) where the cell constant, d/a (cm^{-1}) is the determined from the following equation:

$$\kappa = (d/a)\, L$$

The conductivity of the ionic liquids was measured at several temperatures, multiplying the measured conductivity by the cell constant to determine the specific conductivity.

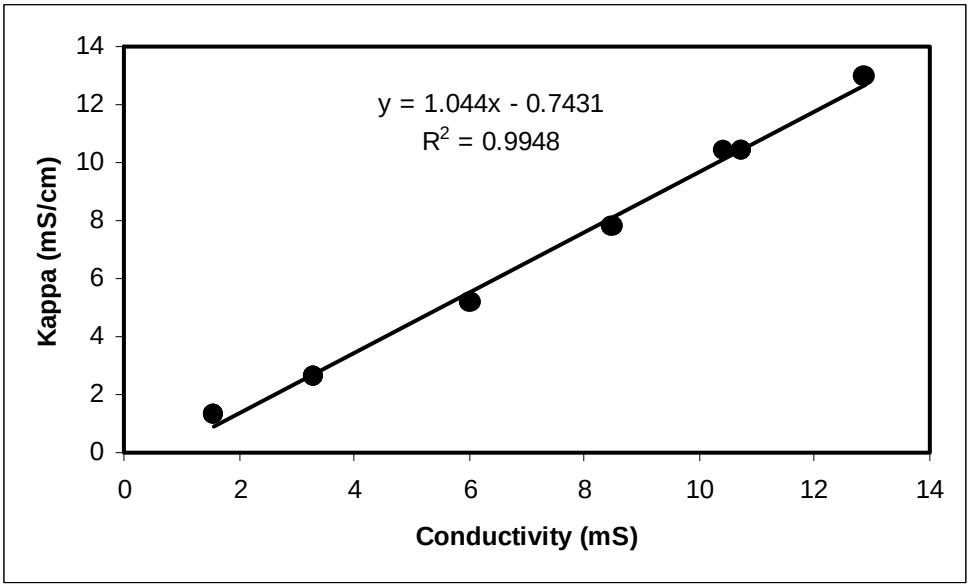


Figure 11. The calibration of a conductivity probe used to measure the conductivity of the ionic liquids.

Electrochemical Properties

The electrochemical potential windows of the ionic liquids were measured using a Princeton Applied Research Potentiostat/Galvanostat (Model 173) with a EG&G Parc Universal Programmer (Model 175). The analog data was converted to digital data using a MacLab/4 Analog Digital Instruments interface. The data was recorded digitally using Scope V3.1 software, running on a Macintosh operating system. Approximately 1 mL of ionic liquid was placed into a miniature electrochemical cell. A glassy carbon electrode was used as the working electrode, a Ag|AgCl electrode served as the reference electrode, and a Pt wire as a counter electrode. Sensitivities were set at 10 μA/V and the scan rate was set to 100 mV/s.

Synthesis

Preparation of 1-ethyl-3-methylimidazolium chloride (EMICl):

1-Ethyl-3-methylimidazolium chloride was synthesized by reacting 1-chloroethane and N-methylimidazole in a heavy walled, safety coated pressure bottle manufactured by Ace Glass Co.. Inside of a nitrogen filled glove bag, 1.30 moles (81.28 g) of 1-chloroethane were condensed into a pressurized bottle using a liquid nitrogen/ethanol bath at approximately -30 ^{o}C (Figure 12). Then 1.02 moles (83.75 g) of distilled N-methylimidazole was added. The bottle was sealed using a Teflon threaded stopper, removed from the glove bag, and stirred in an oil bath set at 45-50 ^{o}C. After a few hours, two layers of liquid formed. The progress of the reaction was monitored by the size of the two layers forming in the bottle. After approximately eight days, the reaction flask was removed from the oil bath and placed into the freezer until crystals of EMICl were formed. The crystals were dissolved in acetonitrile and recrystallized with ethyl ether. The ethyl ether was decanted and the crystals were dried in a vacuum overnight then stored in a dessicator until further use. Typical yields were near 95%.

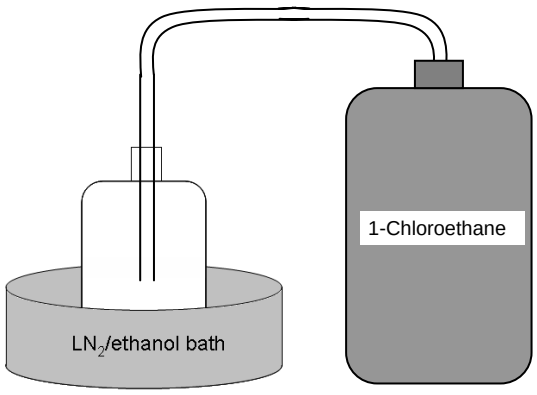


Figure 12. The setup for the condensation and reaction of 1-chloroethane with N-methylimidazole.

Preparation of 1-ethyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)-imide (EMIBeti):

1-Ethyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide was prepared from EMICl and LiBeti using a simple ion exchange reaction. EMICl (~82 grams) was dissolved in approximately 200 mL of water then an equimolar amount of lithium bis((pentafluoroethane)sulfonyl)imide (LiBeti) dissolved in water (200 mL) was added. The solution immediately turned cloudy and two layers of water and EMIBeti began to form. The solution was allowed to stir overnight. The resulting ionic liquid was then placed in a separatory funnel where the aqueous phase containing dissolved LiCl was removed from the ionic liquid phase. LiCl was completely removed from the ionic liquid by washing it with 40 mL portions of deionized water (20-30 times) until the aqueous phase did not test positive for Cl^- when reacted with $AgNO_3$. Following the removal of the chloride, the ionic liquid was dried on a high vacuum line (5×10^{-4} mmHg) to remove any residual water. The structure and purity of the ionic liquid were confirmed using ^1H NMR and ^{13}C NMR. ^1H peaks were found at δ 8.92 (s, 1H), 7.72 (t, 1H), 7.64 (t, 1H) 4.38 (m, 2H), 4.026 (s, 3H), and 1.562 (t, 3H) ppm. It is believed that the multiplets found in the 7.6 – 7.7 ppm range are the result of coupling between the hydrogen atoms bonded to the carbon atoms of the ring.

Preparation of 1-propyl-3-methylimidazolium chloride (PMICl):

Using a nitrogen filled glove bag, 0.54 moles (42.5 g) of 1-chloropropane was added to 0.53 moles (43.5 g) of distilled N-methylimidazole (a 1% excess of 1-chloropropane) in a reaction bottle as described in the synthesis of EMICl. The bottle was sealed and removed from the glove bag, then placed in an oil bath at 45-50 ^oC and

stirred for eight days. As before, the progress of the reaction was monitored by the size of the two layers produced. Once the reaction was complete, the reaction flask was cooled in the freezer to promote PMICl crystal formation. Ethyl ether (~50 mL) was added to further enhance crystal formation. The percent yield was near 77%.

Preparation of 1-propyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)-imide (PMIBeti):

1-Propyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide was prepared in a similar manner to EMIBeti. PMICl (68.62 g) was dissolved in approximately 100 mL of deionized water and an equimolar amount of LiBeti (165.72 g) in deionized water was added. The solution turned cloudy immediately and was allowed to stir overnight. The resulting ionic liquid was then washed with 20 mL portions of deionized water until it tested negative for chloride. The ionic liquid was dried for several hours on a high pressure vacuum line to remove any remaining water. ^{1}H NMR peaks found at δ 9.01 (s, 1H), 7.76 (t, 1H), 7.71 (t, 1H), 4.33 (t, 2H), 4.07 (s, 3H), 1.98 (m, 2H), and 0.97 (t, 3H) ppm confirm the structure and purity of the ionic liquid. ^{13}C-Dept135 spectra also provided confirmation.

Preparation of 1-butyl-3-methylimidazolium chloride (BMICl):

1-Butyl-3-methylimidazolium chloride was prepared in the same manner as PMICl. Typically, a 1% excess of 1-chlorobutane was added to previously distilled N-methylimidazole and allowed to react for approximately 10 days at 45-50 ^{o}C. A longer reaction time was required due to the nature of the chloroalkanes; a longer alkyl chain will decrease the reactivity of the chloroalkane. The solution was then placed into the freezer to promote BMICl crystal growth. Typical yields for this reaction were near 95%.

Preparation of 1-butyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)-imide (BMIBeti):

The same procedure was used to prepare 1-butyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide as was used to produce PMIBeti. ^{1}H NMR peaks found at δ 8.92 (s, 1H), 7.71 (t, 1H), 7.65 (d, 1H), 4.33 (t, 2H), 4.03 (s, 3H), 1.93 (m, 2H), 1.39 (m, 2H), and 0.95 (t, 3H) ppm confirmed the structure and purity of the ionic liquid. ^{13}C-Dept135 spectra also confirmed the structure and purity.

Preparation of 1-pentyl-3-methylimidazolium chloride (PnMICl):

1-Pentyl-3-methylimidazolium chloride was synthesized following the same procedure as PMICl by reacting a 1% excess of 1-chloropentane (65.0 g) with N-methylimidazole (45.3 g). After 10-14 days, the reaction flask was cooled by putting it into the freezer. The product, PnMICl was obtained as a very viscous liquid that did not crystallize. The unreacted liquid was decanted before any further reaction. Typical yields were around 75%.

Preparation of 1-pentyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)-imide (PnMIBeti):

1-Pentyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide was prepared in a similar manner to PMIBeti. ^{1}H NMR peaks found at δ 8.97 (s, 1H), 7.74 (t, 1H), 7.68 (t, 1H), 4.34 (t, 2H), 4.04 (s, 3H), 1.95 (m, 2H), 1.35 (m, 4H), and 0.89 (t, 3H) ppm confirmed the structure and purity in addition to ^{13}C-Dept135 spectra.

Preparation of 1-hexyl-3-methylimidazolium chloride (HMICl):

1-Hexyl-3-methylimidazolium chloride was prepared in the same manner as PMICl. In a typical synthesis, a 10% molar excess of 1-chlorohexane (49.4 g) was added

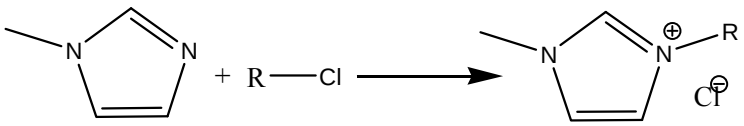
to distilled N-methylimidazole (30.6 g) and allowed to react for approximately 14 days at 45-50 ^{o}C. It also formed a very viscous liquid. Any unreacted material was decanted before further reaction. This reaction produced an 86% yield.

Preparation of 1-hexyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)-imide (HMIBeti):

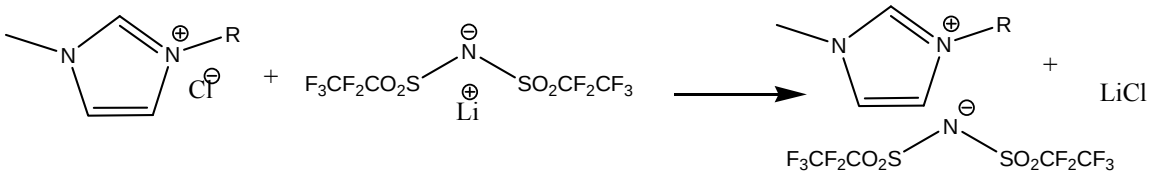
The same procedure was used to produce 1-hexyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide as was used to produce PMIBeti. The structure and purity were confirmed using ^{1}H NMR. Peaks were found at δ 8.97 (s, 1H), 7.74 (t, 1H), 7.67 (d, 1H), 4.05 (t, 2H), 4.34 (s, 3H), 1.96 (m, 2H), 1.36 (m, 6H), and 0.88 (t, 3H) ppm. ^{13}C-Dept135 spectra also confirmed the structure and purity.

III. RESULTS AND DISCUSSION

In this study, 1-alkyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide ($Beti^-$) ionic liquids, where the alkyl group is an ethyl, propyl, butyl, pentyl, or hexyl, were synthesized. The synthesis involved the formation of 1-alkyl-3-methylimidazolium chloride by the reaction of the corresponding alkyl chloride with N-methylimidazole as shown below:



The second step in the formation of the ionic liquids involved the replacement of the chloride ion with the $Beti^-$ anion:



The syntheses of PMIBeti, PnMIBeti, and HMIBeti have not been previously reported. The physical, thermal, and electrochemical properties of the ionic liquids as a function of alkyl chain length were studied using a variety of techniques described below. Their properties were also compared to some previously synthesized ionic liquids with different anions ($EMIBF_4$, $BMIBF_4$, and $BMIPF_6$). It is believed that the properties such as absorption of water, density, and conductivity will decrease as the alkyl chain length

increases, while the viscosity and electrochemical potential windows will increase with increasing alkyl chain length. It is also suspected that the $Beti^-$ ionic liquids will be less sensitive to moisture and have lower conductivities than BF_4^- or PF_6^- based ionic liquids. A wider potential window, high conductivity, low density, low viscosity, and a low sensitivity to moisture would make them the best candidate for use as an electrolyte in lithium ion batteries.

Absorption and Desorption of Water

Although imidazolium based ionic liquids containing larger alkyl groups are not miscible with water, they will absorb some moisture from the air. The amount of water absorbed by the ionic liquid depends on the relative humidity, the anion, and the length of the alkyl chain in the 1-alkyl-3-methylimidazolium cation.

In this work, 1-alkyl-3-methylimidazolium Beti ionic liquids were exposed to moist air at 60% RH and 25 ^oC. The amounts of water absorbed by the ionic liquids were measured at different time intervals by the Karl Fisher method as described in the experimental. The data are given in Table 8 and shown in Figures 13-17.

Table 8. The maximum amounts of water absorbed by the ionic liquids.

	Maximum Water Content (ppm)
EMIBeti	4050
PMIBeti	4000
BMIBeti	3600
PnMIBeti	3400
HMIBeti	3000

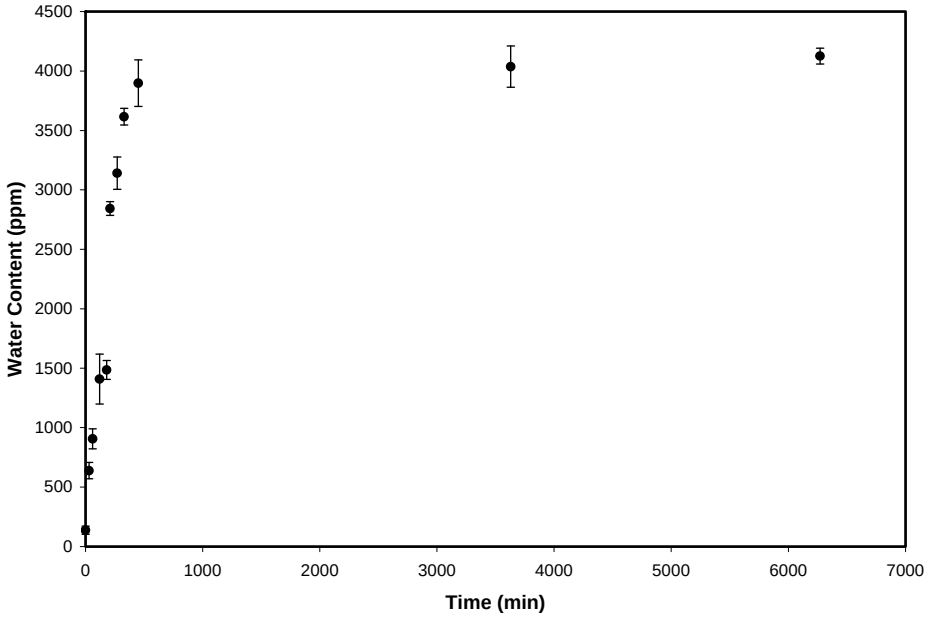


Figure 13. The absorption of water by EMIBeti at 60% RH.

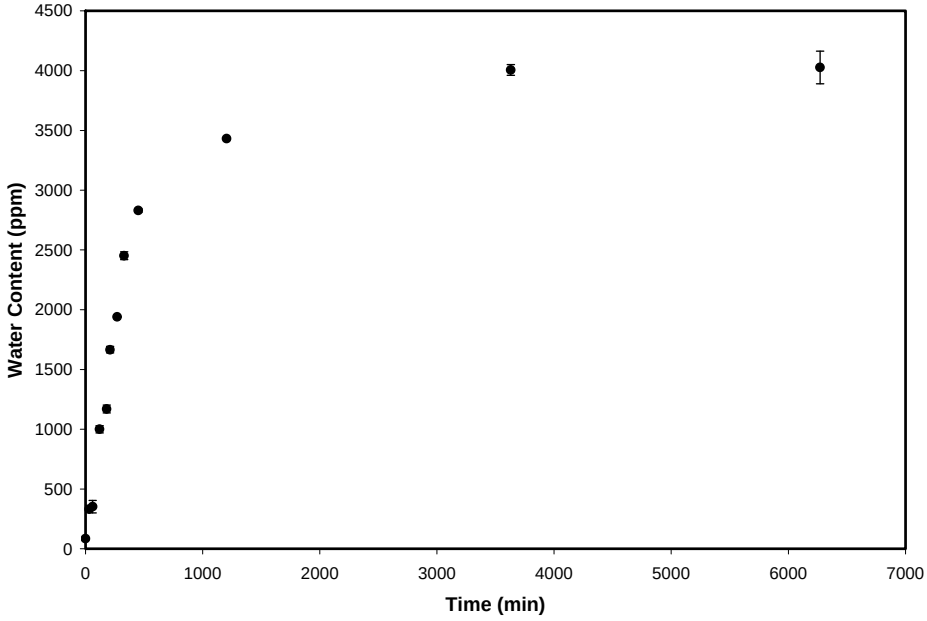


Figure 14. The absorption of water by PMIBeti at 60% RH.

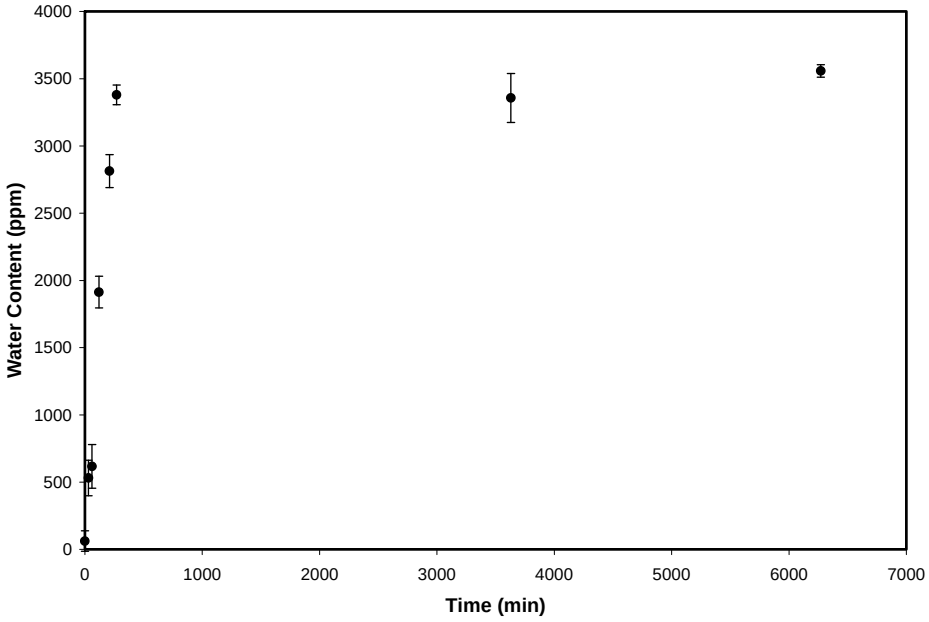


Figure 15. The absorption of water by BMIBeti at 60% RH.

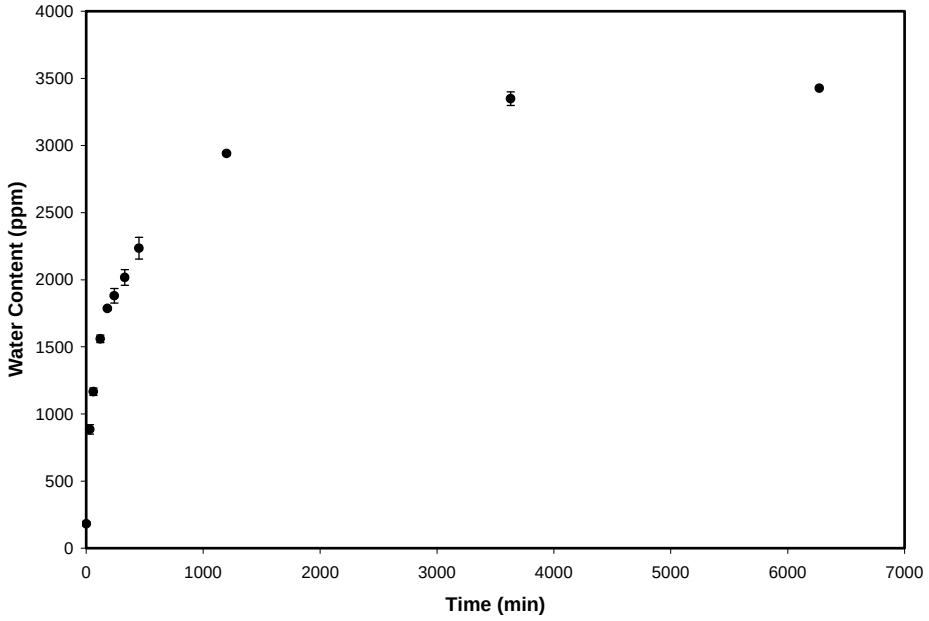


Figure 16. The absorption of water by PnMIBeti at 60% RH.

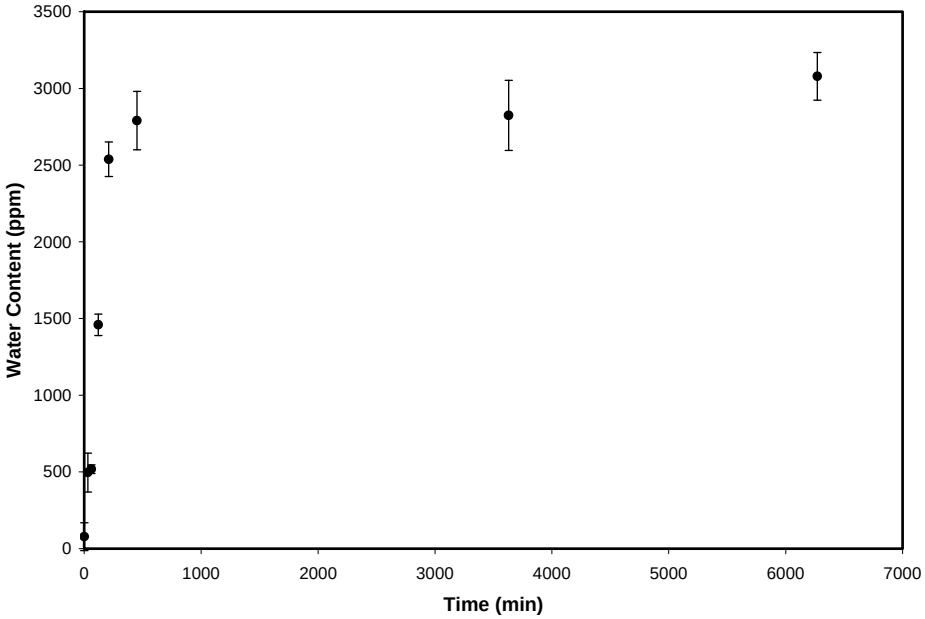


Figure 17. The absorption of water by HMIBeti at 60% RH.

The absorption of water by the ionic liquids with the $Beti^-$ anion showed that the imidazolium cations with shorter alkyl chains tend to absorb more water than those with longer chains. This seems likely as a longer alkyl chain will make the ionic liquid more hydrophobic and also promote cation stacking interactions and hydrogen bonding within the liquid preventing the absorption of water into the system. The relatively low concentration of water absorbed in these samples with the $Beti^-$ anion can also be attributed to the larger anion, which can prevent the absorption of water.[9]

The absorption of water by ionic liquids containing EMI^+ or BMI^+ cations with BF_4^-, PF_6^-, and $Beti^-$ anions were also previously investigated in this laboratory.[25] Ionic liquids containing BF_4^- anions absorb the most water, followed by PF_6^- anions, and then $Beti^-$ anions (Figure 18). This is consistent with previous reports by Cammarata et al. which compared ionic liquids with a BMI^+ cation and a BF_4^-, PF_6^-, or NTf_2^- anion.[45] In Cammarata's work the ionic liquids were exposed to 59% RH for 24 hours. The

maximum amount of water absorbed by each ionic liquid is given in Table 9. It would appear that the fluoroethyl group on the $Beti^-$ anion prevents water absorption more than that of the fluoromethyl substituent of NTf_2^-. This seems likely as the fluoroethyl group is larger and more electronegative than its fluoromethyl relative which would assist in the prevention of water absorption. Also, the $Beti^-$ anion is capable of strong dipole interactions due to the presence of the fluorine atoms which would also prevent the absorption of water.

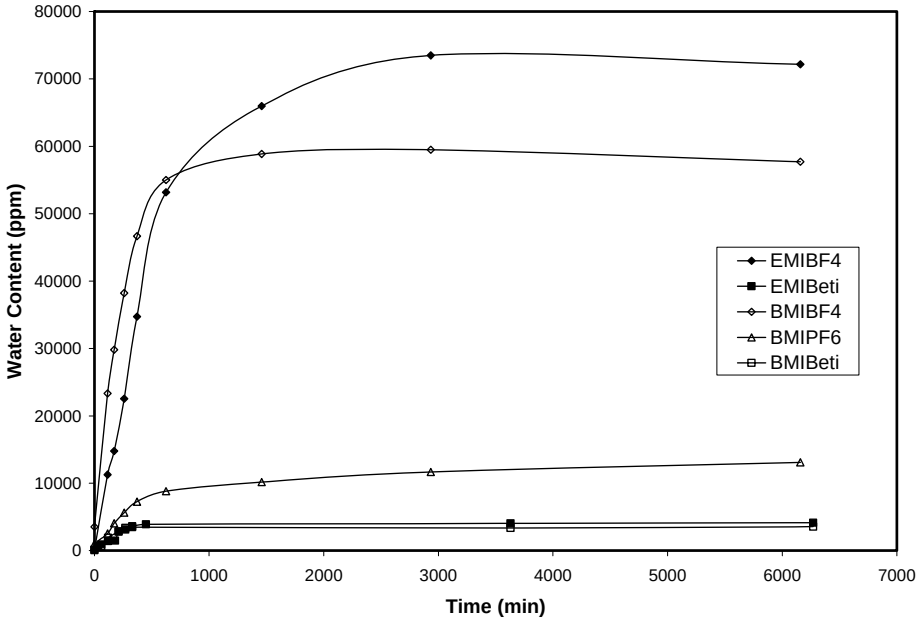


Figure 18. The effects of differing anions on the absorption of water

Table 9. Water content of ionic liquids as published by Cammarata et al.

	Water Content (ppm)
$BMIPF_6$	2640
$BMIBF_4$	19500
$BMITf_2N$	3300

It was previously found in this research group that ionic liquids will desorb water when exposed to a drier environment.[14] The desorption of water from the ionic liquids when exposed to 6% RH seemed to be fairly consistent throughout the series with the exception of PMIBeti which seemed to retain more water than the others for a longer period of time (Figures 19-23). The other four ionic liquids seemed to lose a significant amount of water after being exposed to 6% RH for about eight hours, where it took the PMIBeti much longer to do so.

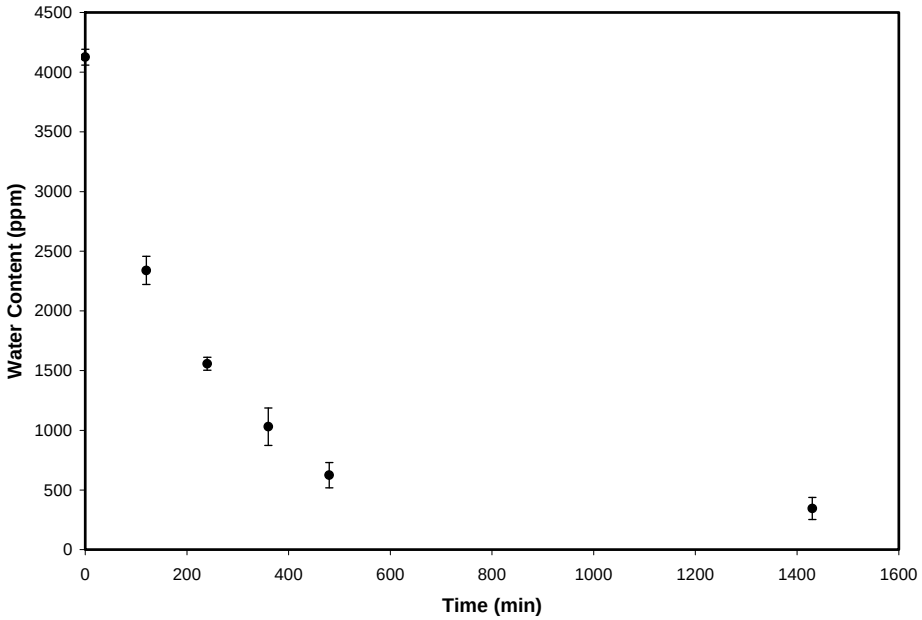


Figure 19. The desorption of water by EMIBeti at 6% RH.

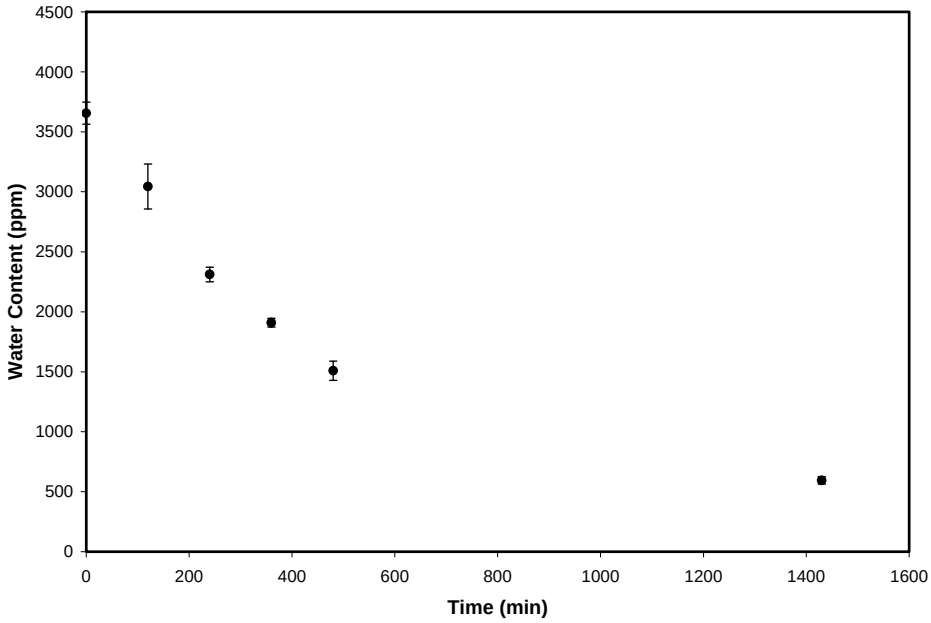


Figure 20. The desorption of water by PMIBeti at 6% RH.

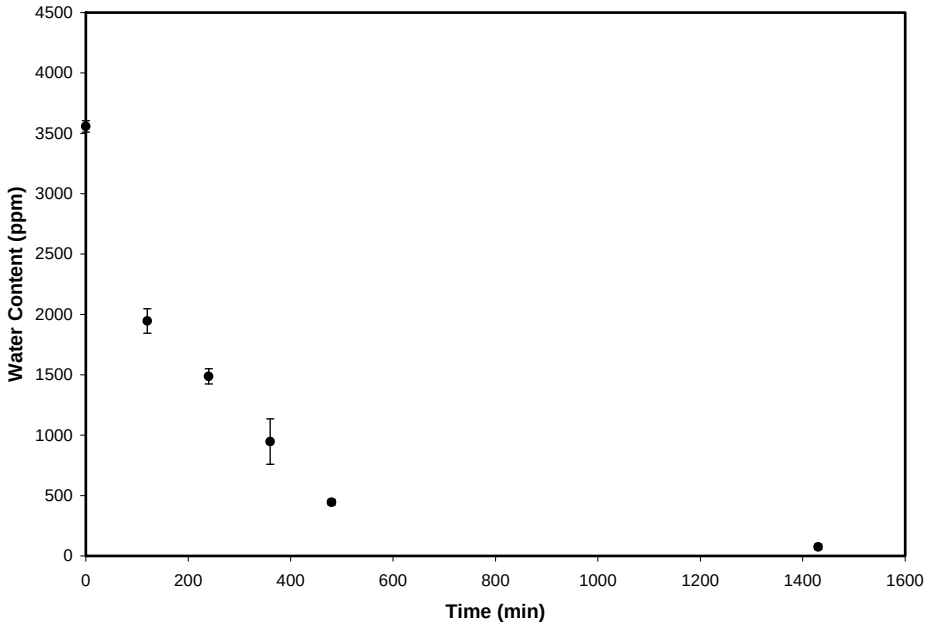


Figure 21. The desorption of water by BMIBeti at 6% RH.

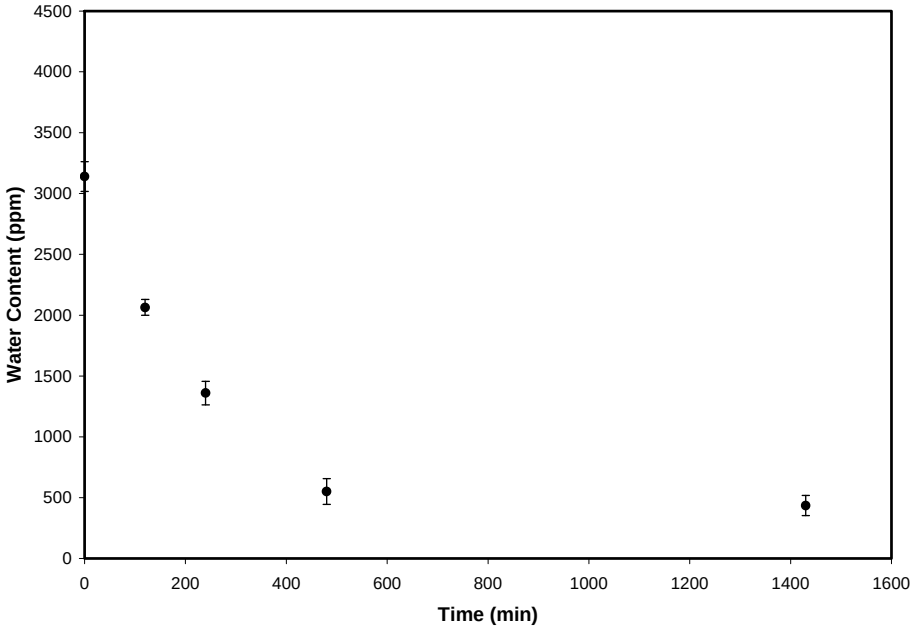


Figure 22. The desorption of water by PnMIBeti at 6% RH.

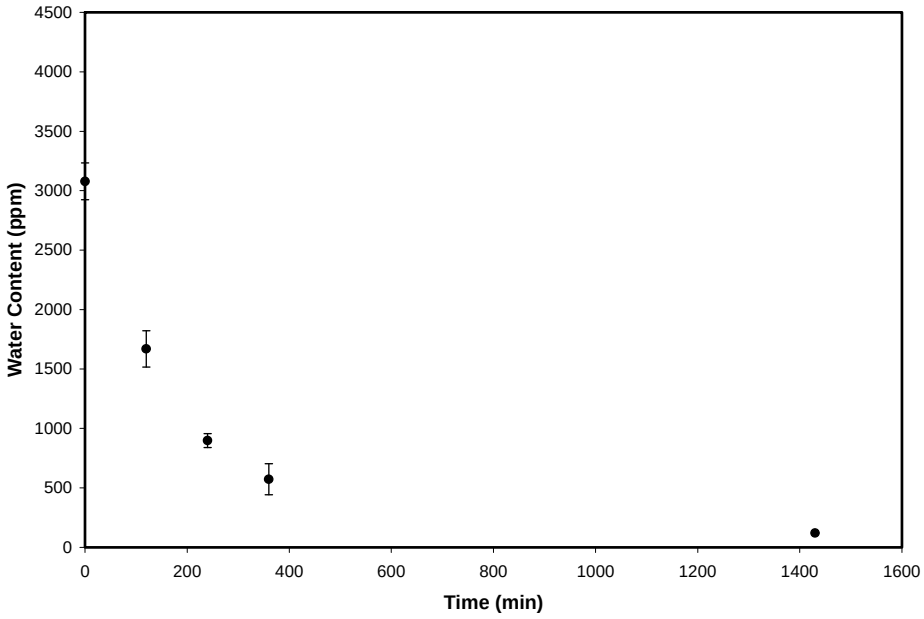


Figure 23. The desorption of water by HMIBeti at 6% RH.

In comparing the behavior of 1-alkyl-3-methylimidazolium ionic liquids with different anions in the desorption of water, it appears that the ionic liquids containing the BF_4^- anion lose water at a much quicker rate than the ionic liquids containing PF_6^- or $Beti^-$ anions (Figure 24). It also appears that the BF_4^- and PF_6^- ionic liquids tend to retain more water after their initial decline than the $Beti^-$ ionic liquids. This seems reasonable considering the BF_4^- and PF_6^- ionic liquids would not form as tight of a lattice as the $Beti^-$ ionic liquids due to the decreased van der Waals interactions in the BF_4^- and PF_6^- ionic liquids. Also, BF_4^- and PF_6^- are more hydrophilic than $Beti^-$ allowing them to retain more water in a drier atmosphere.

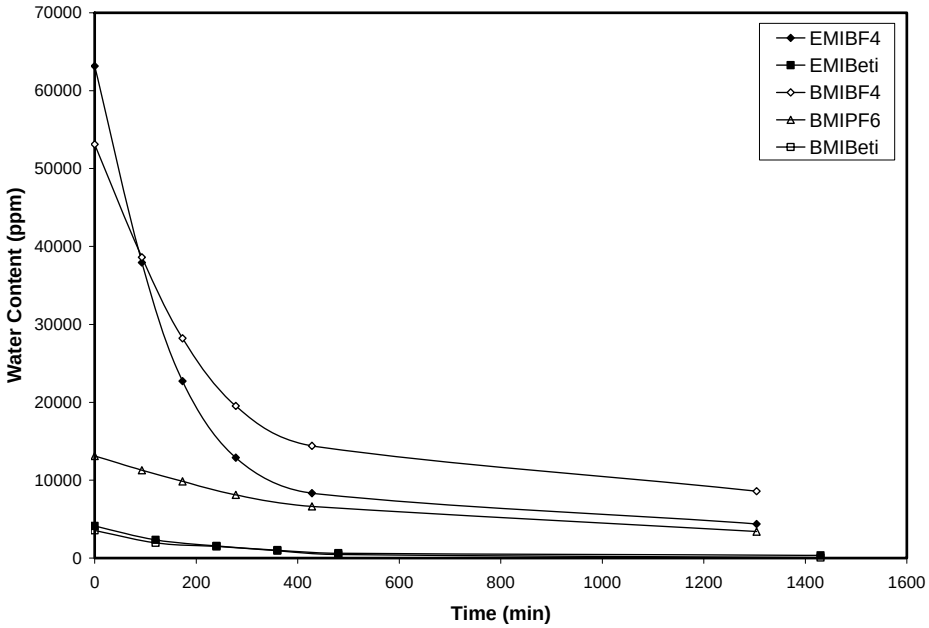


Figure 24. The effects of differing anions on the desorption of water

Water Absorption Studies by Infrared Spectroscopy

Infrared spectroscopy was used to determine the molecular state of the water that was absorbed by the ionic liquid. The vibrational modes of water are very sensitive to

their surrounding environment and to intermolecular interactions in the IR region.[45] In the past, the stretching modes of water have been used to determine the interactions of water in liquid, solid, and vapor phases as well as the interactions between water and other molecules. There are three major bands associated with the vibrations of monomeric water. The first can be found in the 1595 – 1650 cm^{-1} range and corresponds to the bending mode of water (ν_2).[45] However, this band is not definite when determining the state of water. The other two major stretching bands are found in the 3000–3800 cm^{-1} region of the spectrum and can been seen in Figure 25. The peak on the far left due to asymmetric stretching (ν_3) and the peak next to it on the right is due to symmetric stretching (ν_1). As the concentration of water increases the water begins to polymerize, forming hydrogen bonds between several molecules forming a broad peak, characteristic of hydrogen bonding.[45]

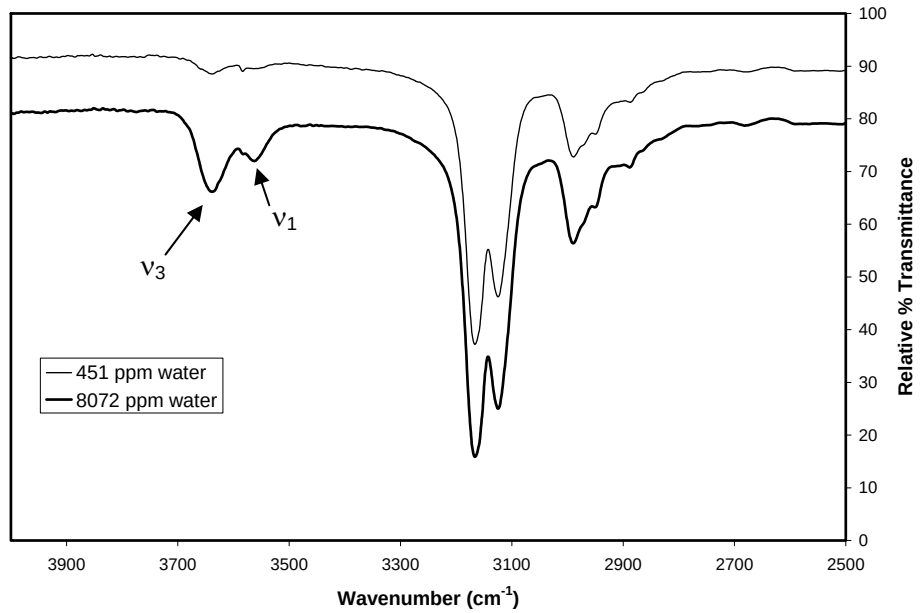


Figure 25. The IR spectrum of $EMIBF_4$ showing the ν_1 and ν_3 stretches of water absorbed by the ionic liquid.

The ionic liquids studied here show the presence of monomeric water at low concentrations in EMIBeti and PMIBeti; that is, the water molecules are not hydrogen bonded with themselves but rather with the cation and anion of the ionic liquid (Figures 26-27). In BMIBeti, PnMIBeti, and HMIBeti the presence of polymeric water did begin to form with higher concentrations of water (Figures 28-30). Expanded spectra can be seen in the Appendix.

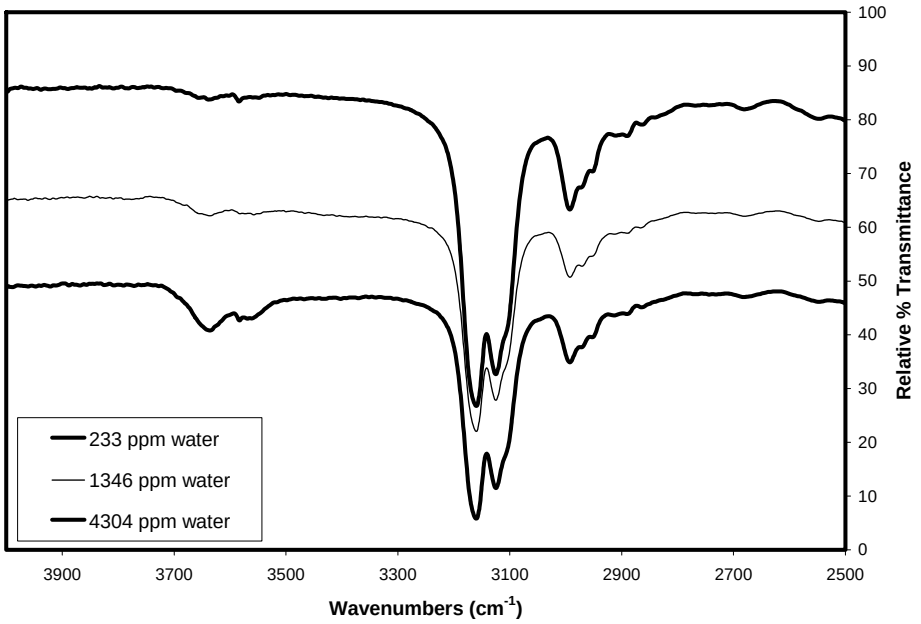


Figure 26. The IR spectra showing monomeric water absorption bands for EMIBeti.

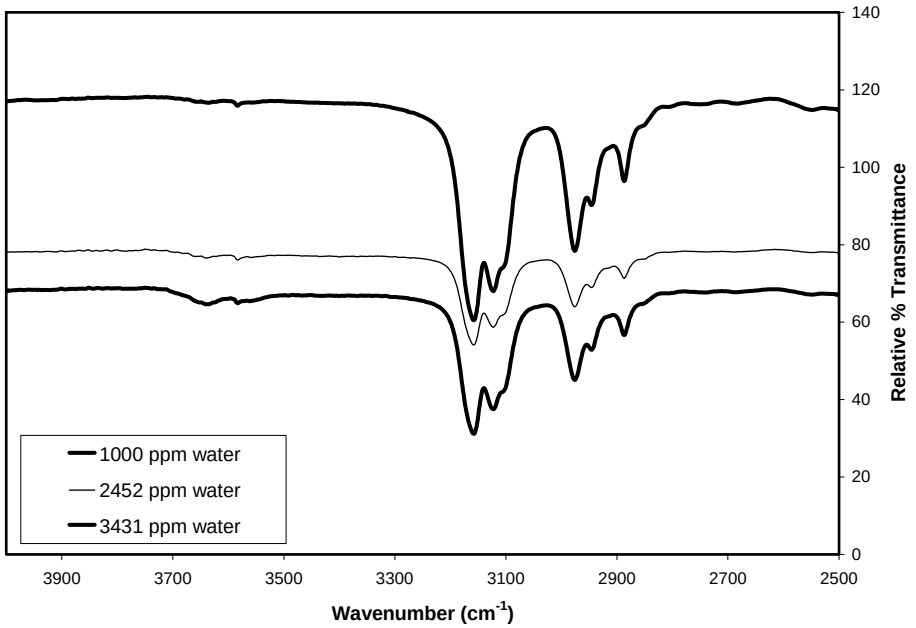


Figure 27. The IR spectra showing monomeric water absorption bands for PMIBeti.

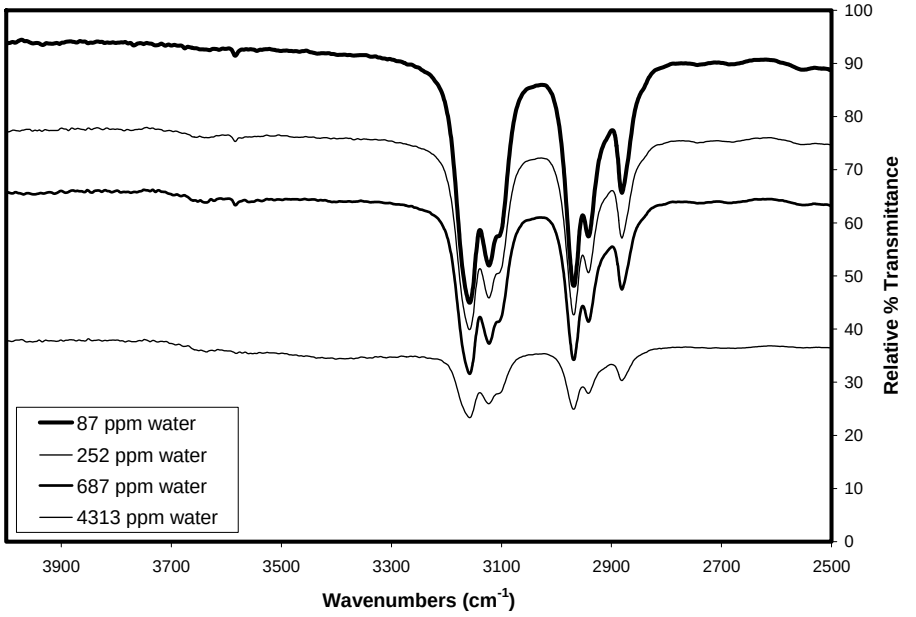


Figure 28. The IR spectra showing polymeric water absorption bands for BMIBeti.

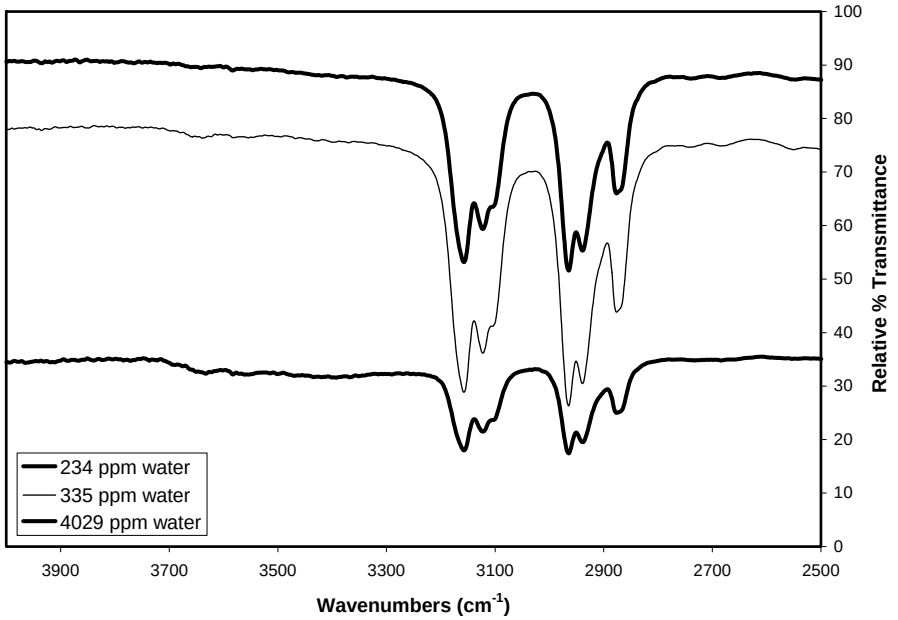


Figure 29. The IR spectra showing polymeric water absorption bands for PnMIBeti.

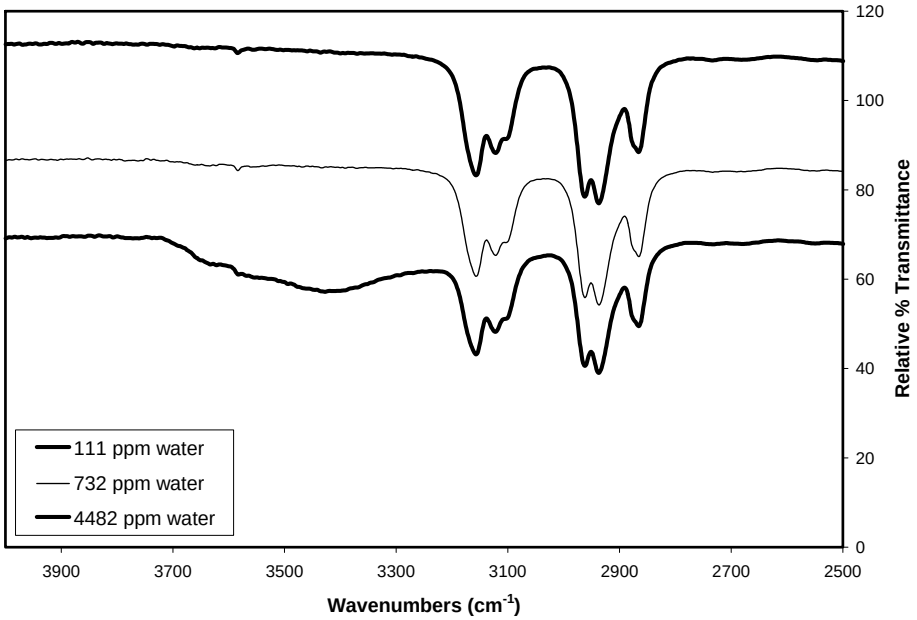


Figure 30. The IR spectra showing polymeric water absorption bands for HMIBeti.

Density

The density measurements of the ionic liquids studied were found to be more dense than water and most organic solvents, with values ranging from 1.4 to 1.6 g/mL (Table 10). The density of the ionic liquids decreased as both the chain length and temperature increased (Figure 31), which is consistent with previous reports.[7, 10, 19] At each temperature studied EMIBeti was the most dense of the ionic liquids studied and HMIBeti was the least. The fact that the longer alkyl chains have lower densities is most likely due to the alkyl chain interactions in each ionic liquid; the longer chains would allow for ordering of the ions which would lead to them being less dense because they can slide around each other more easily.

Table 10. Density values for the ionic liquid series at different temperatures (in g/mL).

	H_2O Content	20°C	30°C	40°C	50°C
EMIBeti	178.8	1.597 ± 0.001	1.581 ± 0.003	1.589 ± 0.001	1.415 ± 0.001
PMIBeti	84.6	1.555 ± 0.001	1.551 ± 0.005	1.542 ± 0.002	1.521 ± 0.001
BMIBeti	80.3	1.507 ± 0.001	1.508 ± 0.005	1.499 ± 0.001	1.482 ± 0.002
PnMIBeti	97.7	1.481 ± 0.001	1.480 ± 0.001	1.471 ± 0.001	1.456 ± 0.001
HMIBeti	93.3	1.445 ± 0.003	1.448 ± 0.003	1.434 ± 0.001	1.428 ± 0.001

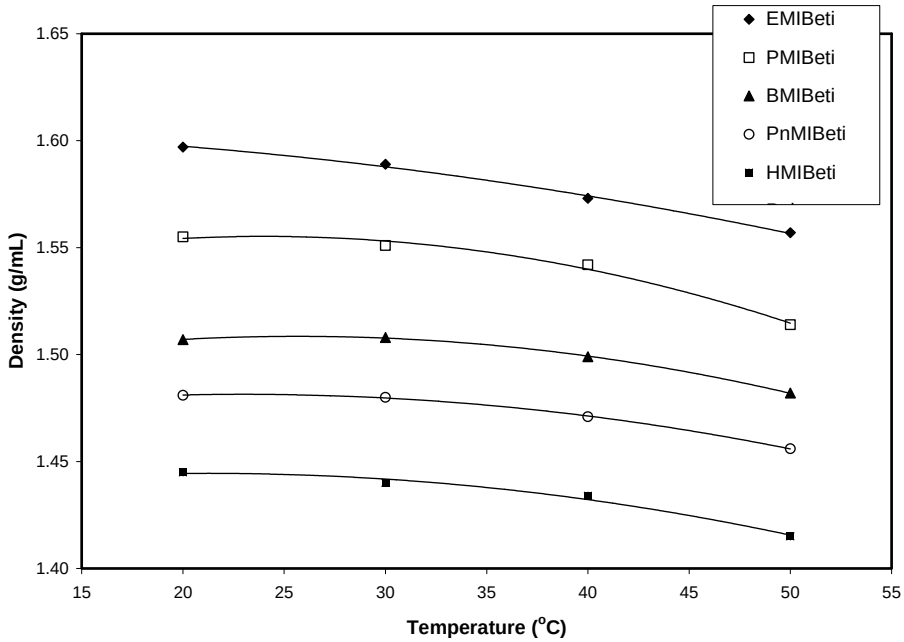


Figure 31. The density of the ionic liquids decreased with increasing temperature and chain length.

Viscosity

The kinematic viscosities of the ionic liquids, EMIBeti, PMIBeti, BMIBeti, PnMIBeti, and HMIBeti, were measured using a Cannon-Fenske viscometer at 20, 30, 40, and 50 ^{o}C can be seen in Table 11. The kinematic viscosity of the ionic liquids increased with increasing alkyl chain length in a fairly linear fashion. This is consistent with previous reports comparing the viscosities of ionic liquids with increasing alkyl chain lengths[10, 23] but in contrast to Bônhote et al.'s findings that showed a decrease then an increase in viscosity for chain lengths of 1 – 4 on 1-alkyl-3-methylimidazolium NTf_2 ionic liquids.[23] The kinematic viscosities decreased with increasing temperature as well (Figure 32). This is as expected as higher temperatures allow for faster flow rates of most substances.

Table 11. Kinematic viscosity values for the ionic liquid series at different temperatures (in mm^2/s).

	H_2O Content	20°C	30°C	40°C	50°C
EMIBeti	178.8	66.1 ± 0.2	47.9 ± 1.5	26.77 ± 0.19	19.59 ± 0.28
PMIBeti	84.6	95.3 ± 1.0	68.7 ± 2.8	33.90 ± 0.29	23.75 ± 0.24
BMIBeti	80.3	101.4 ± 0.5	76.2 ± 2.3	36.91 ± 0.14	24.89 ± 0.10
PnMIBeti	97.7	118.3 ± 0.9	75.8 ± 2.2	41.81 ± 0.28	27.58 ± 0.15
HMIBeti	93.3	148.9 ± 1.0	100.6 ± 5.2	45.42 ± 0.35	30.20 ± 0.33

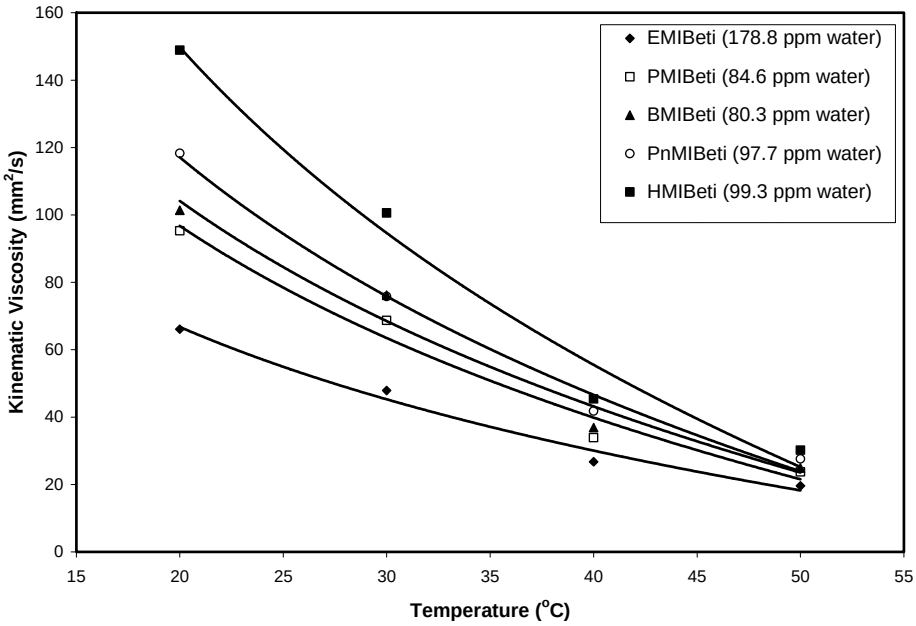


Figure 32. The kinematic viscosity (mm^2/s) of the ionic liquids as a function of temperature.

The absolute viscosities (η), which were found by multiplying the kinematic viscosity by the density of each ionic liquid at the specified temperature, are presented in Table 12. The absolute viscosity was found by. As in the case of the kinematic viscosities, the absolute viscosity increased with increasing chain length and decreased with increasing temperatures. This is consistent with previous reports of similar ionic liquids. The absolute viscosity also showed a trend of decreasing viscosity with increasing temperature which is as expected (Figure 33).

Table 12. Absolute viscosity values for the ionic liquid series at different temperatures (in mPa·s).

	H_2O Content	20°C	30°C	40°C	50°C
EMIBeti	178.8	105.6 ± 0.3	76.2 ± 2.4	42.10 ± 0.29	30.50 ± 0.44
PMIBeti	84.6	148.1 ± 1.5	106.5 ± 4.3	52.28 ± 0.44	36.12 ± 0.36
BMIBeti	80.3	152.1 ± 0.8	114.4 ± 4.4	55.32 ± 0.21	36.88 ± 0.15
PnMIBeti	97.7	175.2 ± 1.3	112.2 ± 3.3	61.49 ± 0.41	40.16 ± 0.22
HMIBeti	93.3	214.1 ± 1.4	145.7 ± 7.5	65.12 ± 0.50	43.14 ± 0.47

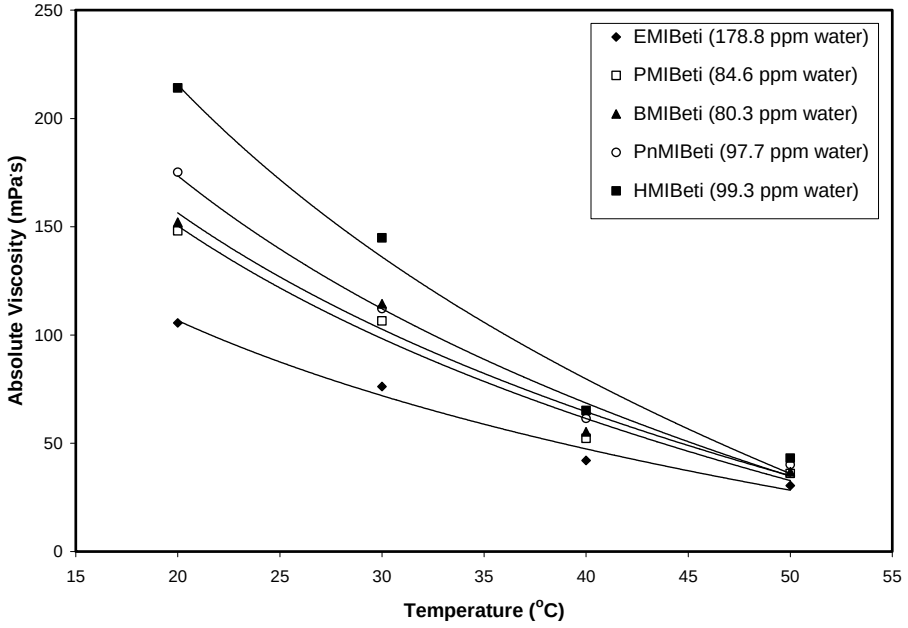


Figure 33. The absolute viscosity (mPa·s) of the ionic liquids as a function of temperature.

Thermal Properties of the Ionic Liquids

Thermal gravimetric analysis was performed on each of the ionic liquids. The start temperature (T_{start}) was taken to be the temperature where the ionic liquid started to decompose. The onset temperature (T_{onset}) is the temperature at the intersection of the baseline weight and the tangent of the curve where decomposition occurs (Figure 34).[8] BMIBeti had the lowest T_{start} at 314 °C while EMIBeti had the highest at 325 °C (Table 13). Analysis shows that all of the ionic liquids are stable up to 400 °C, if not higher.

HMIBeti had the lowest T_{onset} at 405 ^{o}C while PnMIBeti had the highest at 425 ^{o}C. These values seem to coincide with literature values for similar compounds such as $BMINTf_2$ which has a T_{start} of 330 ^{o}C and a T_{onset} of 422^{o}C.[8] The data show no clear trend in chain length affecting the onset temperature or start temperature for this set of compounds. The spectra can be found in the Appendix.

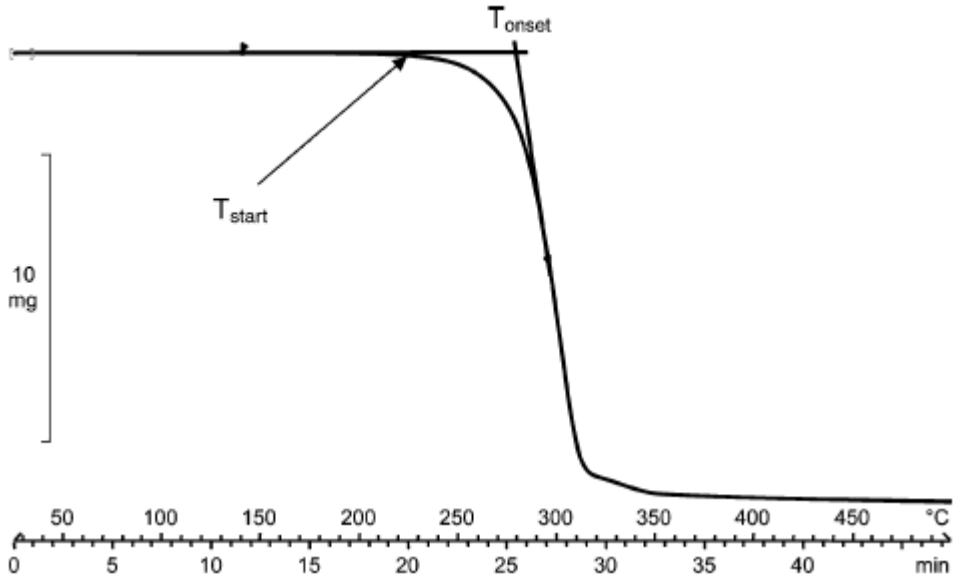


Figure 34. A typical decomposition curve determined by TGA for the imidazolium based ionic liquids showing the T_{start} and T_{onset} values.

Table 13. The T_{start} and T_{onset} values for EMIBeti, PMIBeti, BMIBeti, PnMIBeti, and HMIBeti.

	T_{start} (^{o}C)	T_{onset} (^{o}C)
EMIBeti	325	420
PMIBeti	326	410
BMIBeti	314	410
PnMIBeti	318	425
HMIBeti	321	405

Conductivity

The conductivity of each ionic liquid was measured in the 20 – 140 ^{o}C range. The conductivity of the ionic liquids increased in a polynomial fashion as the temperature increased (Figures 35-39, Tables 14-18). At lower temperatures, the ionic liquids followed a trend of the longer the alkyl chain, the lower the conductivity (Figure 40). At higher temperatures, the conductivities did not seem to follow any trends. The maximum conductivity varied for each of the ionic liquids. Previous reports show the conductivity for EMIBeti to be 3.4 mS/cm[44] and BMIBeti to be 1.9 mS/cm[41] at 26 ^{o}C which correlates to the data reported here showing a conductivity of 3.25 mS/cm for EMIBeti at 21.6 ^{o}C and 1.53 mS/cm for BMIBeti at 22.7 ^{o}C.

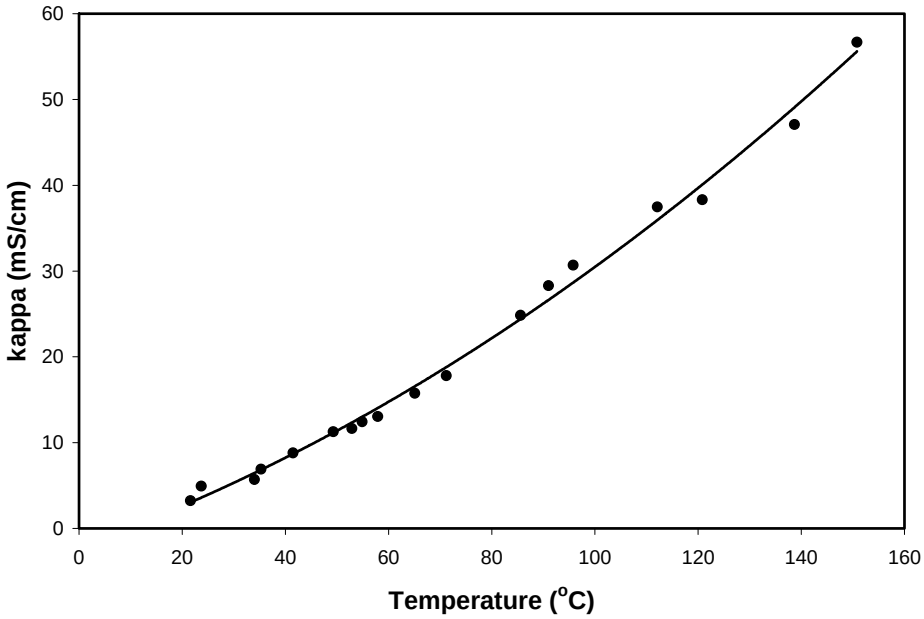


Figure 35. The conductivity curve for EMIBeti.

Table 14. Selected conductivity data for EMIBeti.

Temperature (°C)	Specific Conductivity, κ (mS,cm)
21.6	3.25
34.0	5.70
49.3	11.28
57.9	13.06
65.1	15.75
71.2	1782
85.6	24.85
91.0	28.29
95.8	30.69
112.1	37.48
120.8	38.31
138.7	47.08
150.8	56.69

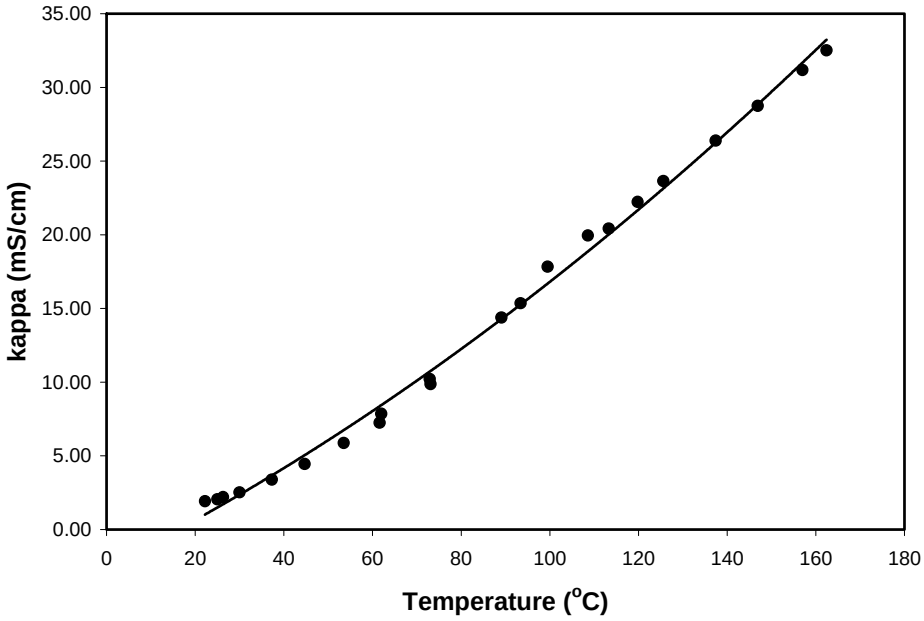


Figure 36. The conductivity curve for PMIBeti.

Table 15. Selected conductivity data for PMIBeti.

Temperature (°C)	Specific Conductivity, κ (mS/cm)
22.2	1.92
26.3	2.20
37.3	3.39
44.7	4.45
53.5	5.88
61.6	7.25
73.1	9.88
89.1	14.39
99.5	17.84
108.6	19.96
119.8	22.24
125.6	23.64
137.4	26.40
146.9	28.76
157.0	31.19
162.4	32.53

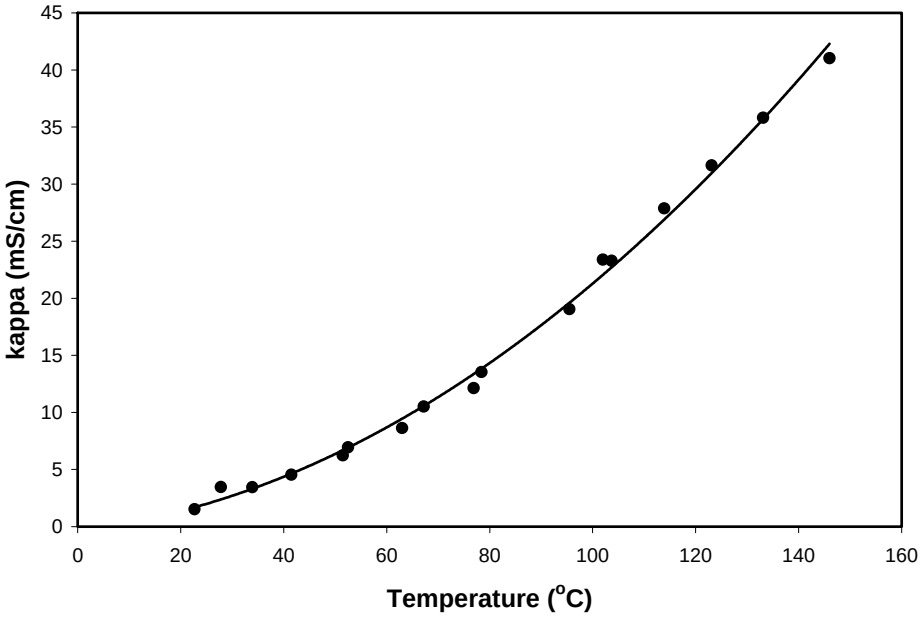


Figure 37. The conductivity curve for BMIBeti.

Table 16. The conductivity data for BMIBeti.

Temperature (°C)	Specific Conductivity, κ (mS/cm)
22.7	1.53
27.8	3.47
33.9	3.45
41.5	4.54
51.5	6.24
52.5	6.95
63.0	8.63
67.2	10.51
76.9	12.13
78.4	13.54
95.5	19.05
102.0	23.39
103.7	23.28
113.9	27.87
123.1	31.63
133.1	35.81
146.0	41.03

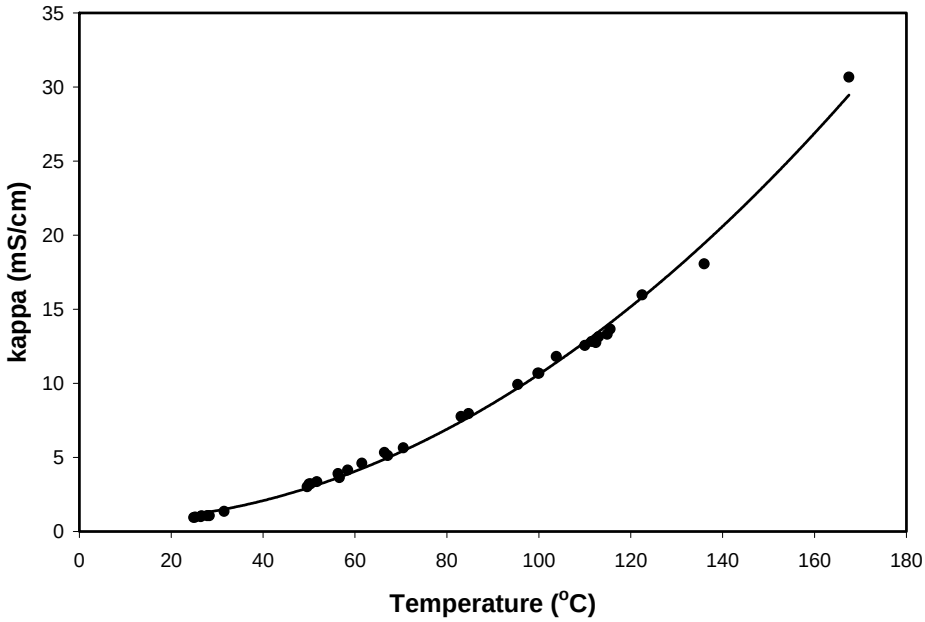


Figure 38. The conductivity curve for PnMIBeti.

Table 17. Selected conductivity data for PnMIBeti.

Temperature (°C)	Specific Conducivity, κ (mS/cm)
24.9	0.94
27.8	1.07
31.5	1.36
49.6	3.02
50.0	3.20
56.3	3.90
66.4	5.33
70.5	5.64
83.1	7.76
95.4	9.91
100.0	10.68
110.0	12.56
112.4	12.76
115.5	13.66
122.5	15.97
136.0	18.07
167.5	30.67

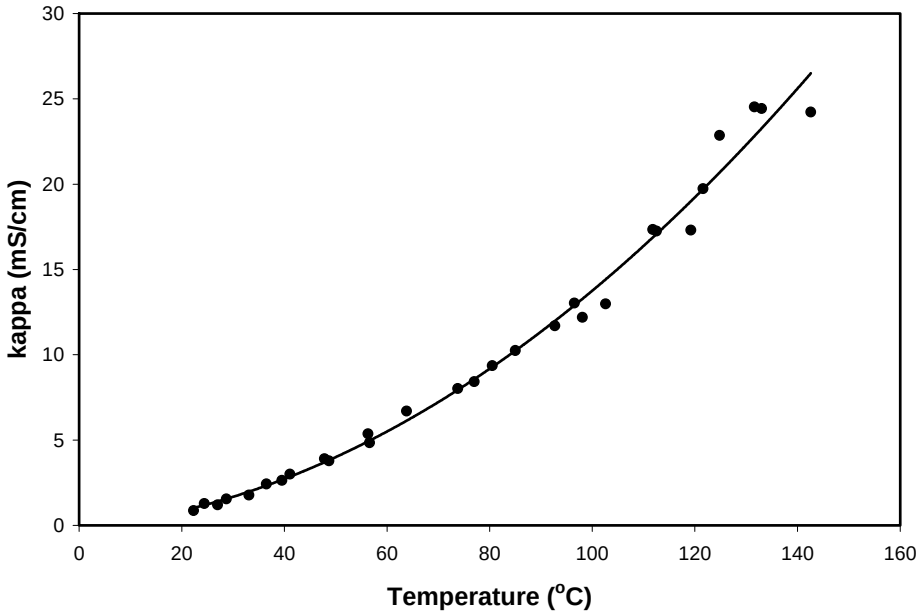


Figure 39. The conductivity curve for HMIBeti.

Table 18. Selected conductivity data for HMIBeti.

Temperature (°C)	Specific Conductivity, κ (mS/cm)
22.3	0.87
27.0	1.20
33.1	1.78
39.5	2.64
47.8	3.92
56.3	5.38
63.8	6.70
73.8	8.02
80.5	9.36
92.7	11.70
96.5	13.04
102.6	12.99
112.5	17.25
119.2	17.31
124.8	22.86
131.6	24.53
133.0	24.43
142.6	24.22

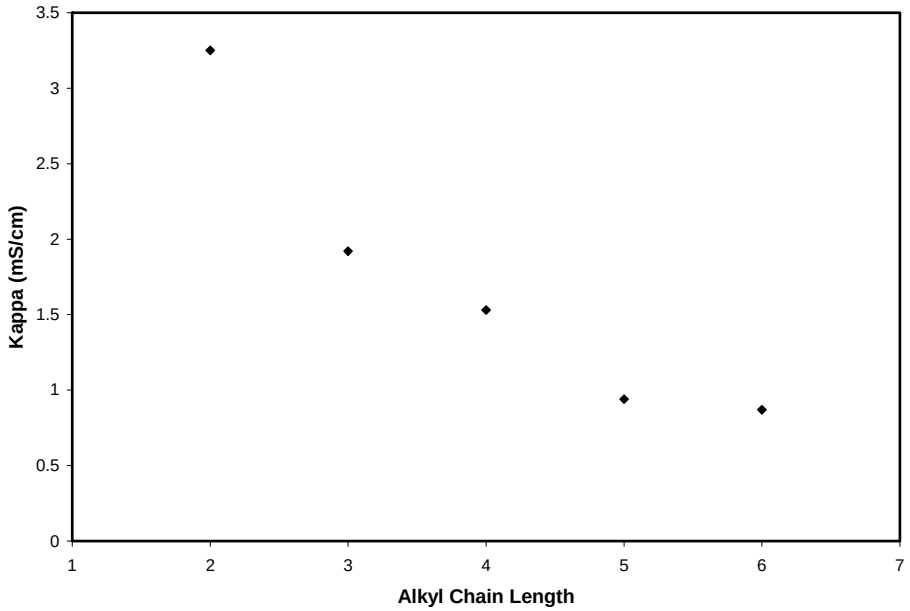


Figure 40. Comparison of the conductivity with increasing alkyl chain length near 20 ^{o}C.

Comparison of data collected for EMIBeti, BMIBeti, $EMIBF_4$[69], and $BMIBF_4$[25] indicate that the $Beti^-$ ionic liquids tend to have lower conductivity than the BF_4^- ionic liquids (Figures 41-42, Tables 19-20). The data for $EMIBF_4$ and $BMIBF_4$ agree quite well with other published values for conductivity near room temperature.[37, 40, 41, 55] EMIBeti and BMIBeti also seems to have a considerably lower conductivity than $EMINTf_2$, whose reported conductivity values range from 5.7 – 8.8 mS/cm near room temperature.[23, 34, 41]

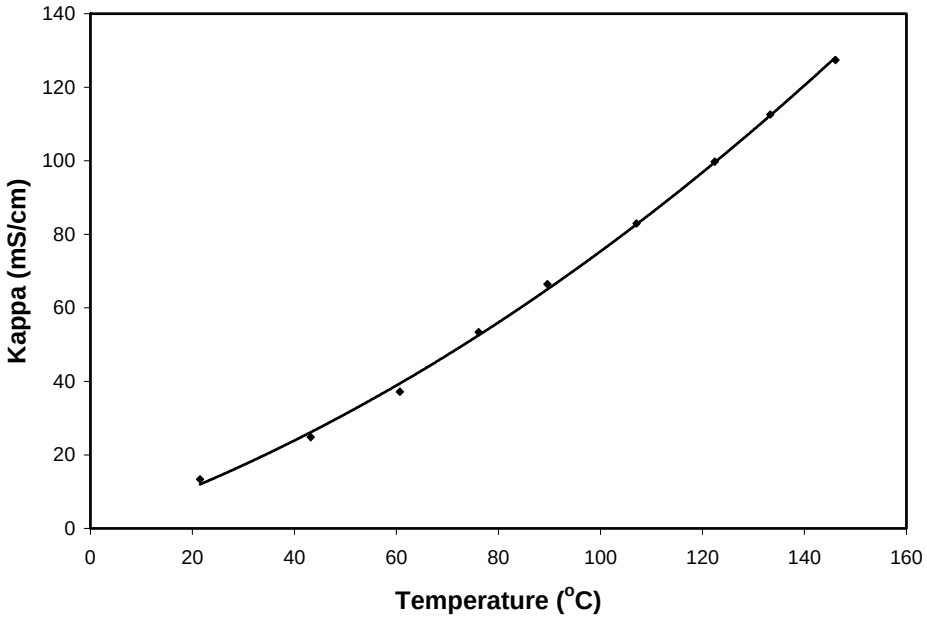


Figure 41. The conductivity curve for $EMIBF_4$.

Table 19. The conductivity data for $EMIBF_4$.

Temperature (°C)	Specific Conductivity, κ (mS/cm)
21.5	13.4
43.2	24.8
60.7	37.2
76.1	53.4
89.6	66.4
107.1	83.0
122.4	99.8
133.3	112.6
146.1	127.4

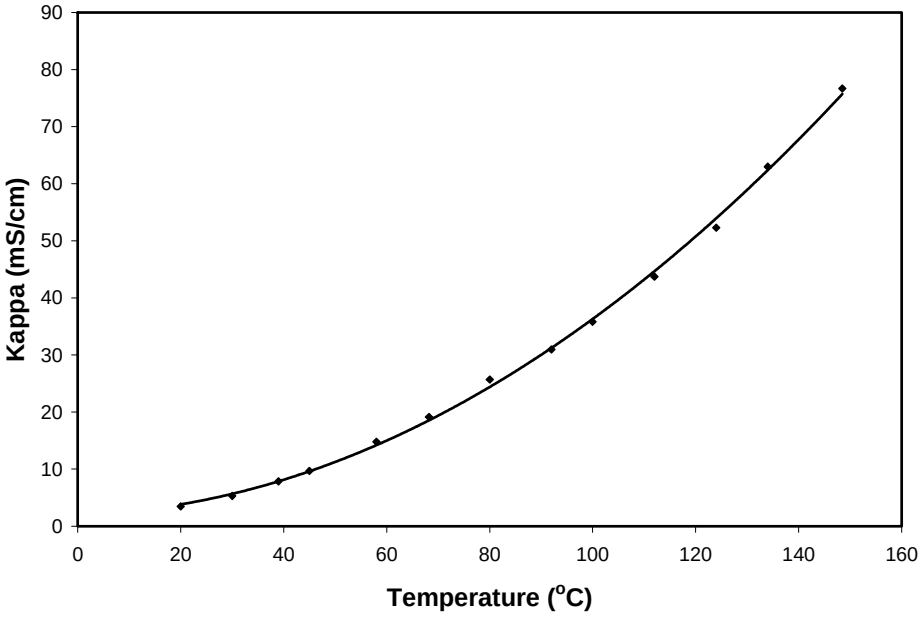


Figure 42. The conductivity curve for $BMIBF_4$.

Table 20. The conductivity data for $BMIBF_4$.

Temperature (°C)	Specific Conductivity, κ (mS/cm)
20.0	3.46
30.0	5.31
39.0	7.85
45.0	9.68
58.0	14.78
68.2	19.14
80.0	25.68
92.0	30.95
100.0	35.83
112.0	43.73
124.0	52.29
134.0	62.98
148.5	78.67

Electrochemical Properties

The electrochemical windows of the 1-alkyl-3-methylimidazolium Beti ionic liquids were determined by cyclic voltammetry using a glassy carbon working electrode, Ag | AgCl reference electrode, and a Pt counter electrode. The ionic liquids containing the $Beti^-$ anion showed a trend of enlarging potential window with increasing alkyl chain length on the 1-alkyl-3-methylimidazolium cation. The cyclic voltammograms are shown in Figure 43 and their specific windows can be seen in Table 21.

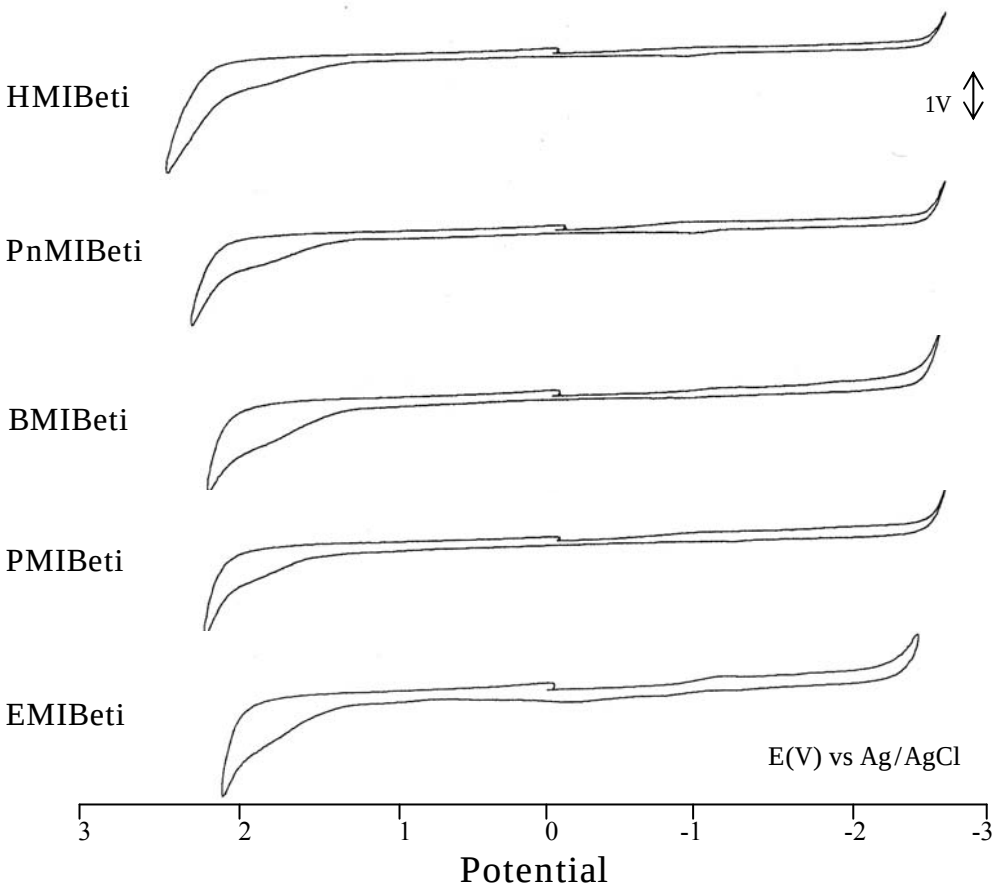


Figure 43. The electrochemical potential windows of the $Beti^-$ ionic liquids studied. The ionic liquids had water concentrations of EMIBeti: 178.8 ppm, PMIBeti: 84.6 ppm, BMIBeti: 80.3 ppm, PnMIBeti: 97.7 ppm, and HMIBeti: 93.3 ppm. The current range was set to 10 μA/V and the scan rate was 100mV/s.

Table 21. The specific potential windows of the $Beti^-$ ionic liquids.

	Positive Potential (V)	Negative Potential (V)	Total Window (V)
EMIBeti	2.0	2.2	4.2
PMIBeti	2.1	2.4	4.5
BMIBeti	2.1	2.4	4.5
PnMIBeti	2.2	2.4	4.6
HMIBeti	2.2	2.5	4.7

The values reported here are comparable or slightly improved over previously reported potential windows for similar compounds. Direct comparison is difficult due to inconsistencies between types of electrodes and traces of impurities. The potential window found for EMIBeti is slightly higher (4.2 V) than previously reported by Wilkes et al.[44] who reported a potential window of 4.1 V using a glassy carbon working electrode and Ag | AgCl reference electrode. The potential reported for HMIBeti is higher than any of the potential windows mentioned earlier.

IV. CONCLUSION

In this study, five new ionic liquids were successfully synthesized. The ionic liquids were composed of a 1-alkyl-3-methylimidazolium cation, where the alkyl chain varied from two to six carbons, and a bis(pentafluoroethylsulfonyl)imide (Beti) anion.

Water absorption studies indicated that these ionic liquids tend to absorb less water than those with a BF_4^- or PF_6^- anion. Also, the amount of water absorbed by the $Beti^-$ based ionic liquids decreases with increasing chain length on the cation. Infrared spectroscopy spectra indicate that the water molecules absorbed by EMIBeti and PMIBeti are monomeric and do not hydrogen bond with additional water molecules. In BMIBeti, PnMIBeti, and HMIBeti, polymeric water begins to form at higher concentrations of water. Water desorption studies show a quick decrease in the amount of water in the ionic liquid at lower humidity which levels out after several hours.

The density of the ionic liquids was also studied. All of the ionic liquids were denser than water, with densities ranging from 1.4 to 1.5 g/mL at ambient temperature. Density was found to decrease with increasing alkyl chain length and with temperature.

The viscosity increased in a fairly linear fashion with increasing chain length. It was also found to decrease with increasing temperatures for the ionic liquid series studied. These trends are consistent with previously reported data.

Thermal gravimetric analysis proved that the ionic liquids were thermally stable up to nearly 400 ^oC which makes them good candidates for use in batteries. Another step

that could be taken to provide further information regarding the thermal stability of these ionic liquids would be to heat them to a higher temperature and hold them there to study their thermal behavior. If the ionic liquids are thermally stable for an extended period of time it would increase their applicability as a battery electrolyte.

The value of the ionic liquids' conductivity increased in a non-linear fashion with increasing temperatures. These ionic liquids loosely followed a trend of the longer the alkyl chain, the lower the conductivity. The ionic liquids were also found to have lower conductivities than those with BF_4^- anions.

1-alkyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide ionic liquids were shown to have electrochemical potential windows in the range of 4.2 – 4.7 V. The potential increased with increasing alkyl chain on the cation. The potential windows reported here are comparable, if not slightly better than potential windows reported for other ionic liquids for use as a battery electrolyte.

There are many more possibilities of further research that can be done with these ionic liquids. Finding the melting and freezing points would be very helpful in order to know their full liquid range. Also, more electrochemical studies should be done to learn more about their electrochemical properties and their ability to act as a battery electrolyte. Knowing more about how water affects the properties of these ionic liquids can be helpful in determining their effectiveness as battery electrolytes.

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VI. APPENDIX

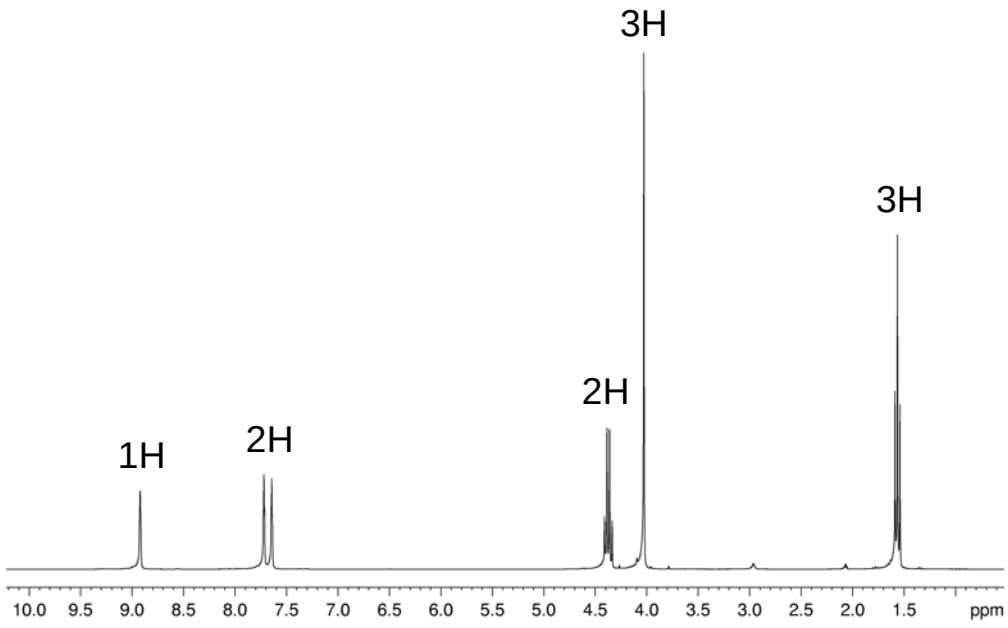

Figure 44. The ^{1}H NMR spectra of EMIBeti.

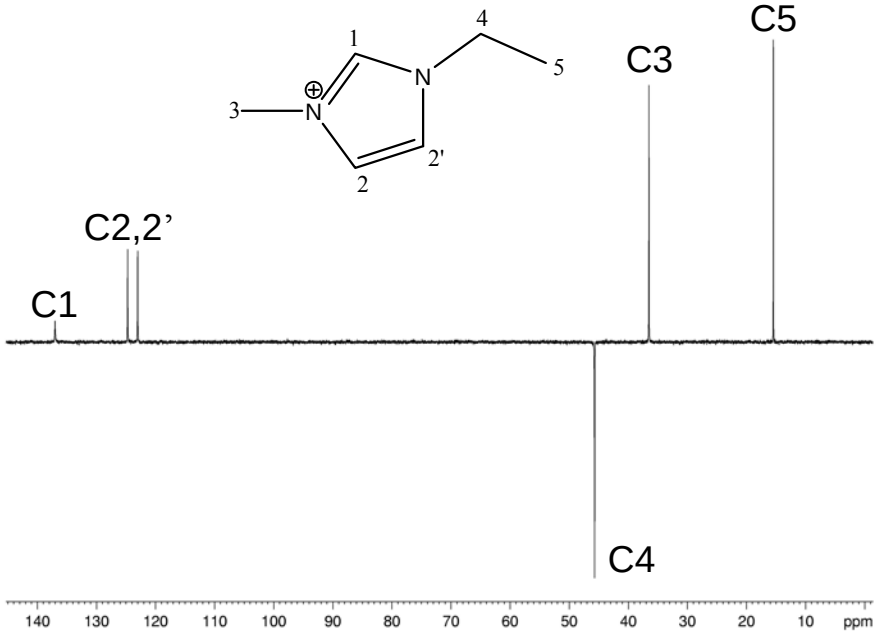

Figure 45. The DEPT-135 spectra of EMIBeti.

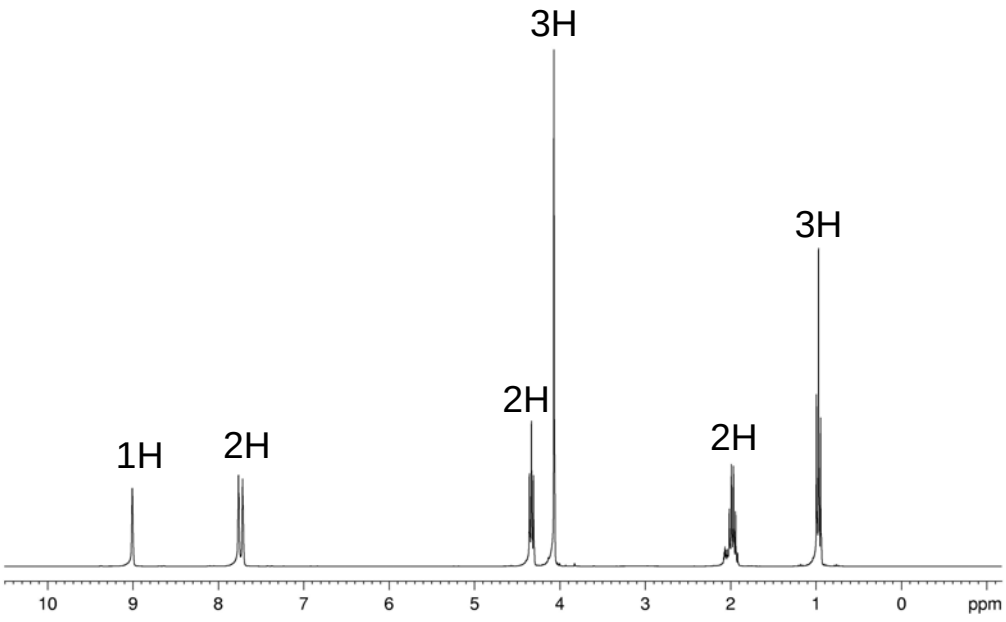

Figure 46. The ^{1}H NMR spectra of PMIBeti.

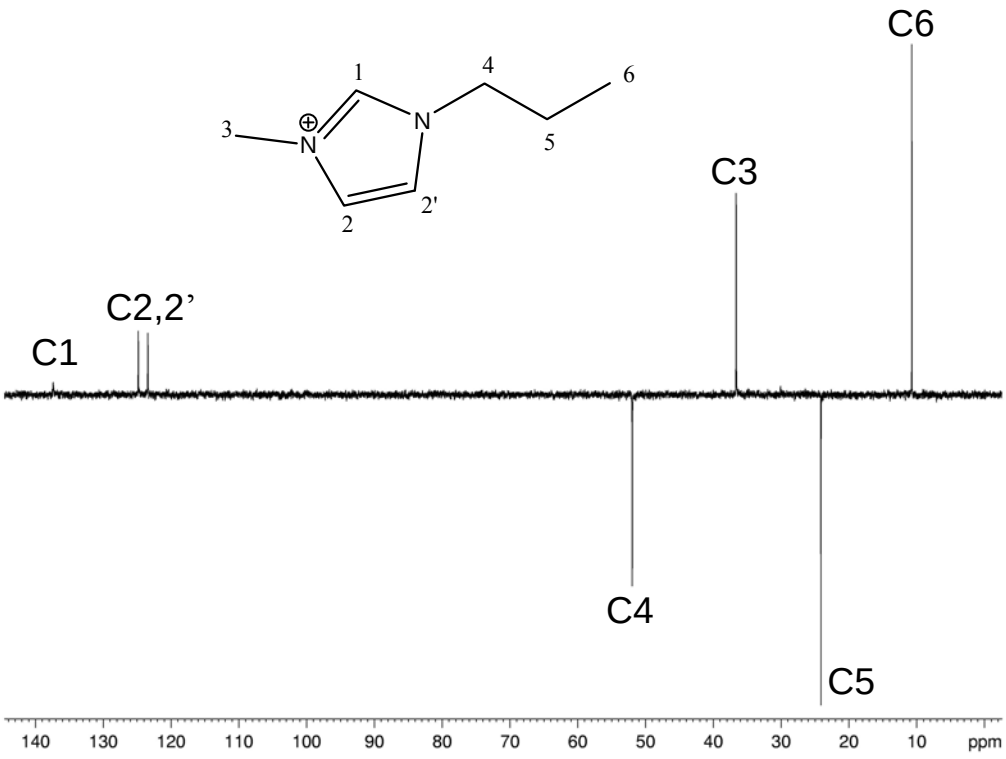

Figure 47. The DEPT-135 spectra of PMIBeti.

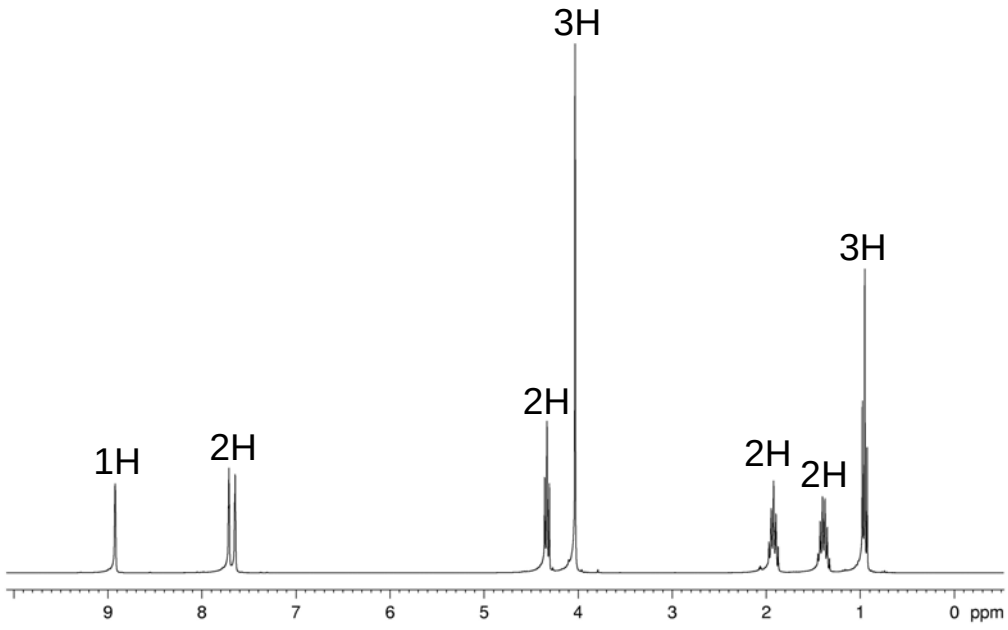

Figure 48. The ^{1}H NMR spectra of BMIBeti.

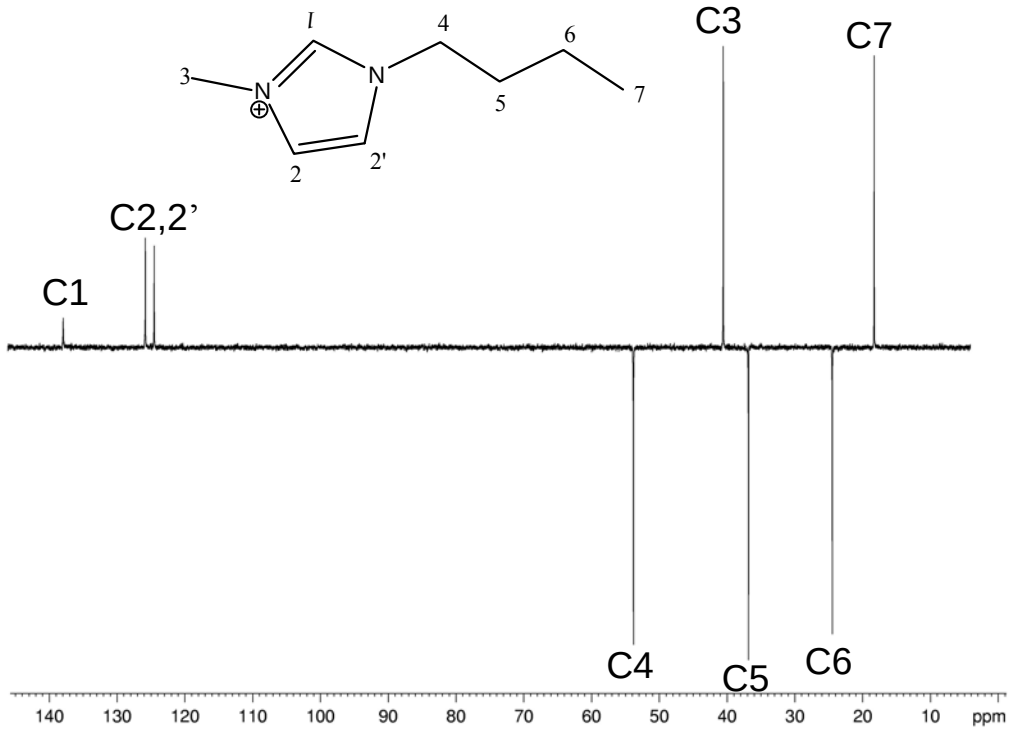

Figure 49. The DEPT-135 spectra of BMIBeti.

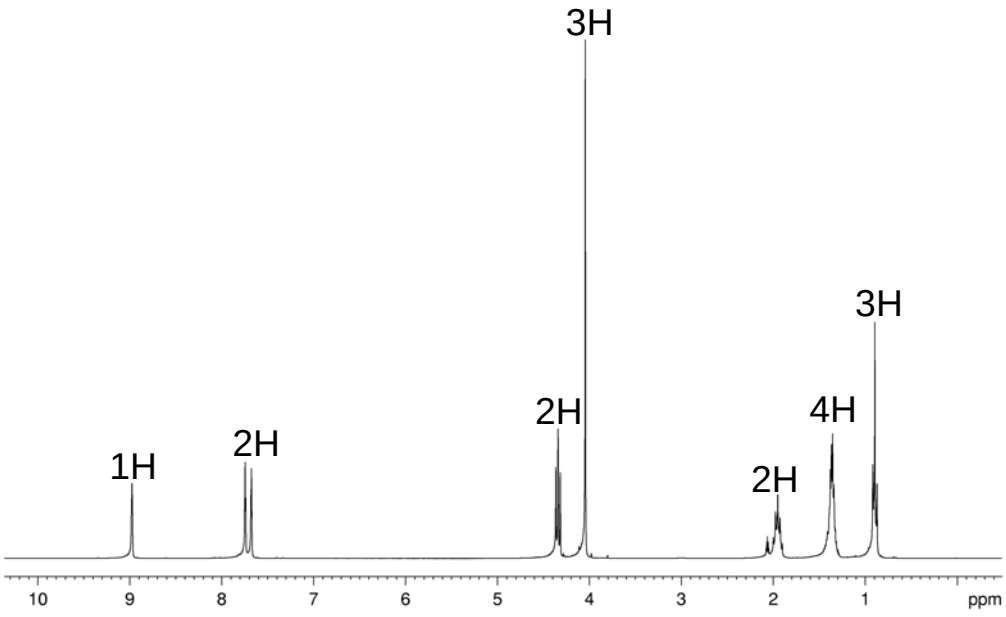

Figure 50. The ^{1}H NMR spectra of PnMIBeti.

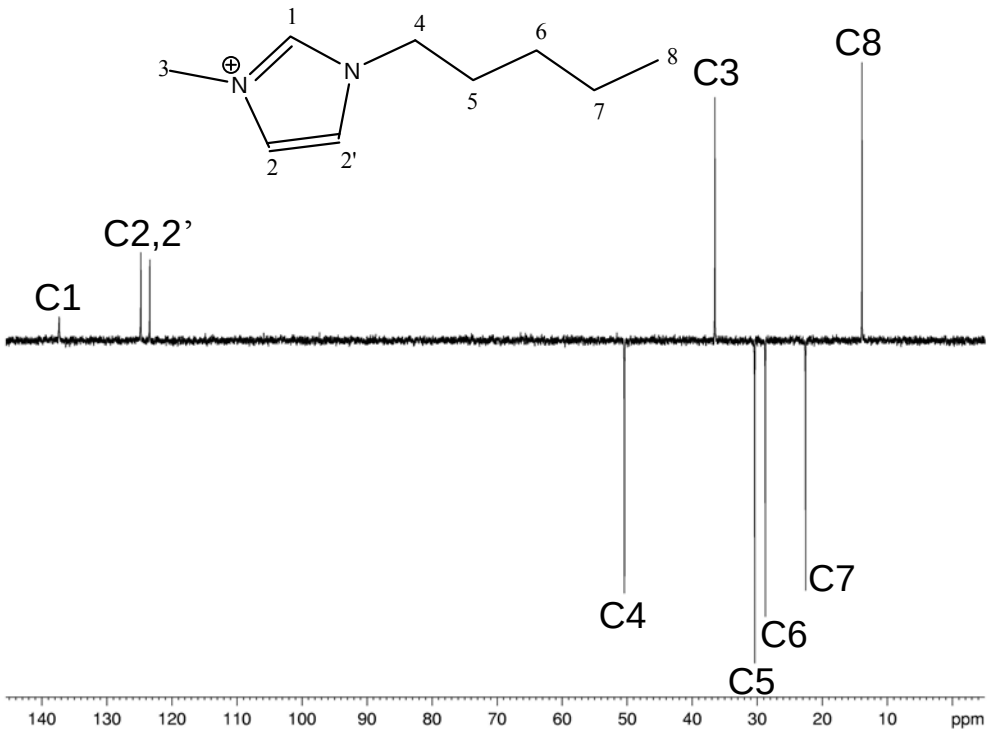

Figure 51. The DEPT-135 spectra of PnMIBeti.

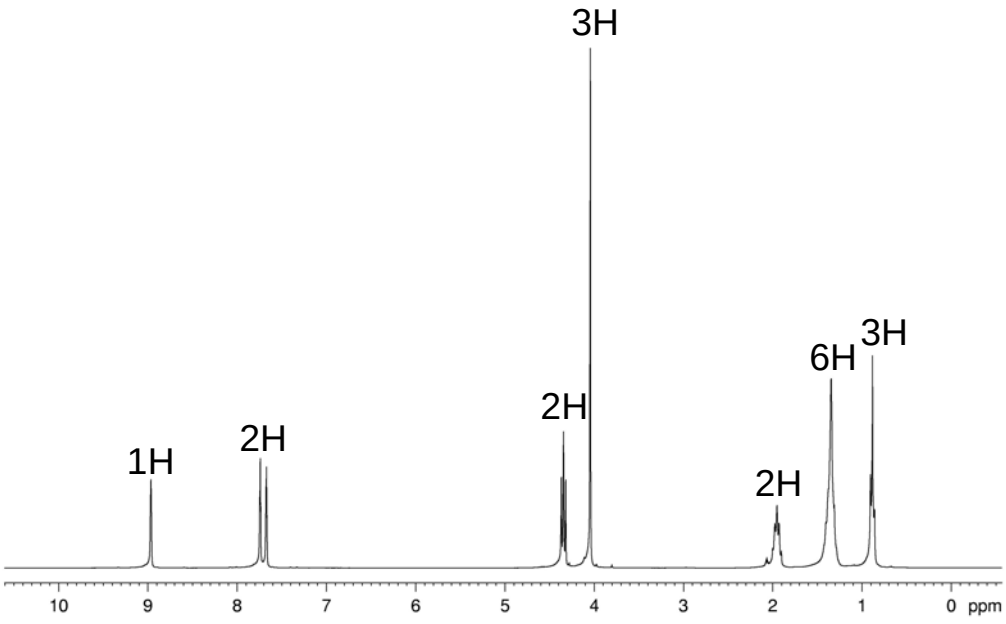

Figure 52. The ^{1}H NMR spectra of HMIBeti.

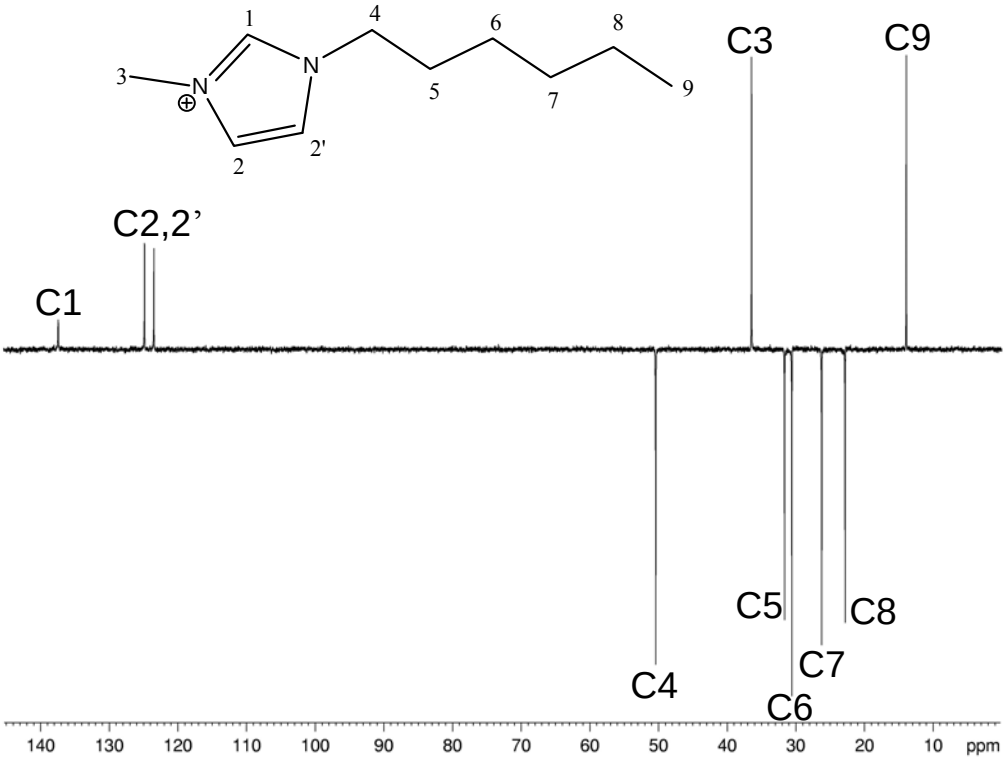

Figure 53. The DEPT-135 spectra of HMIBeti.

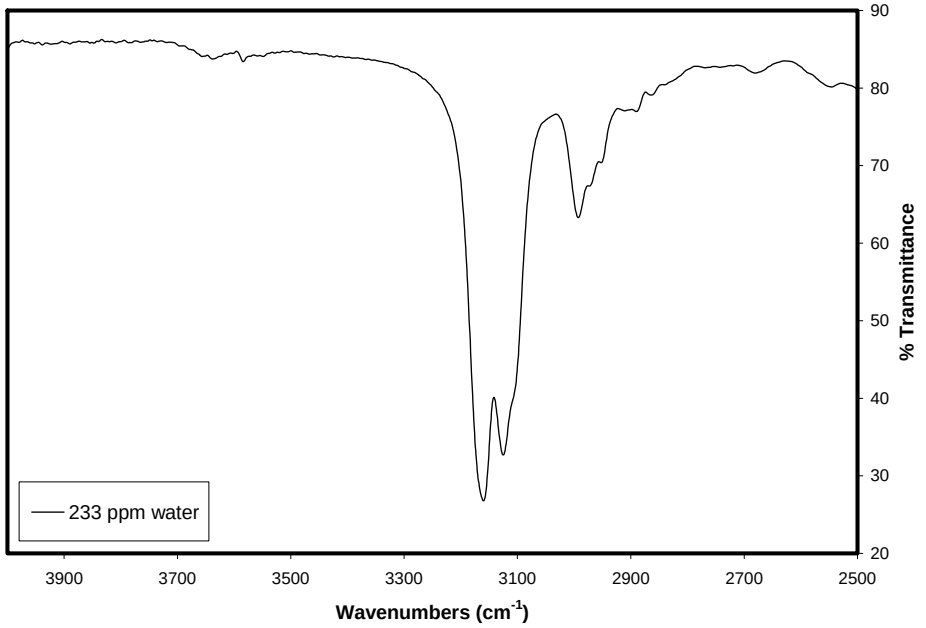

Figure 54. The IR spectra of EMIBeti with 233 ppm water.

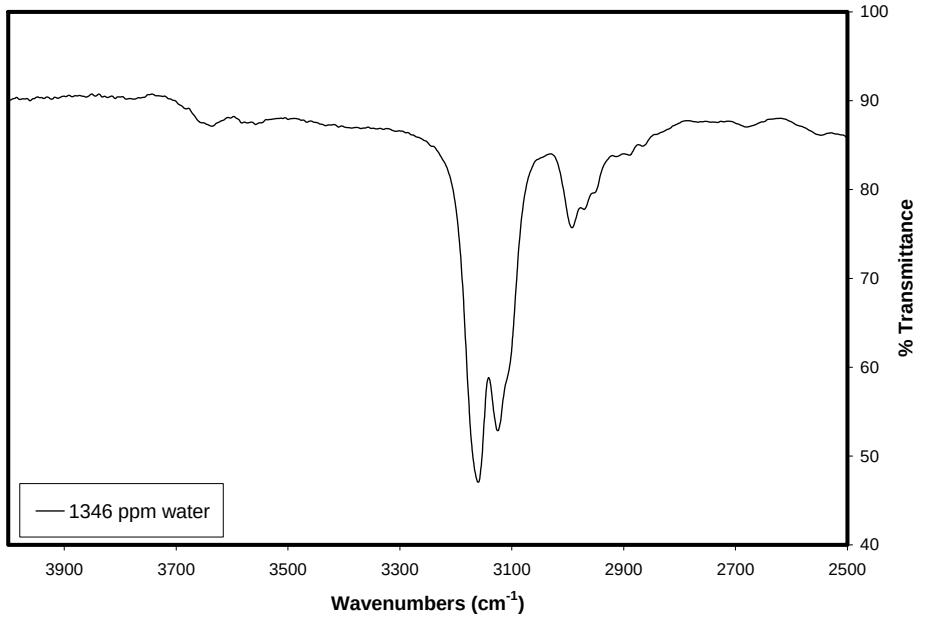

Figure 55. The IR spectra of EMIBeti with 1346 ppm water.

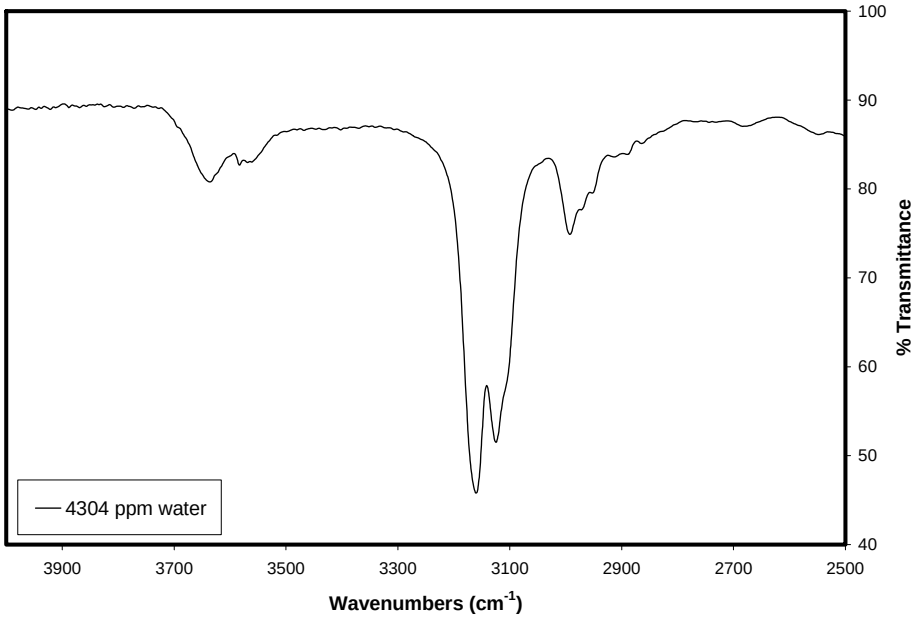

Figure 56. The IR spectra of EMIBeti with 4304 ppm water.

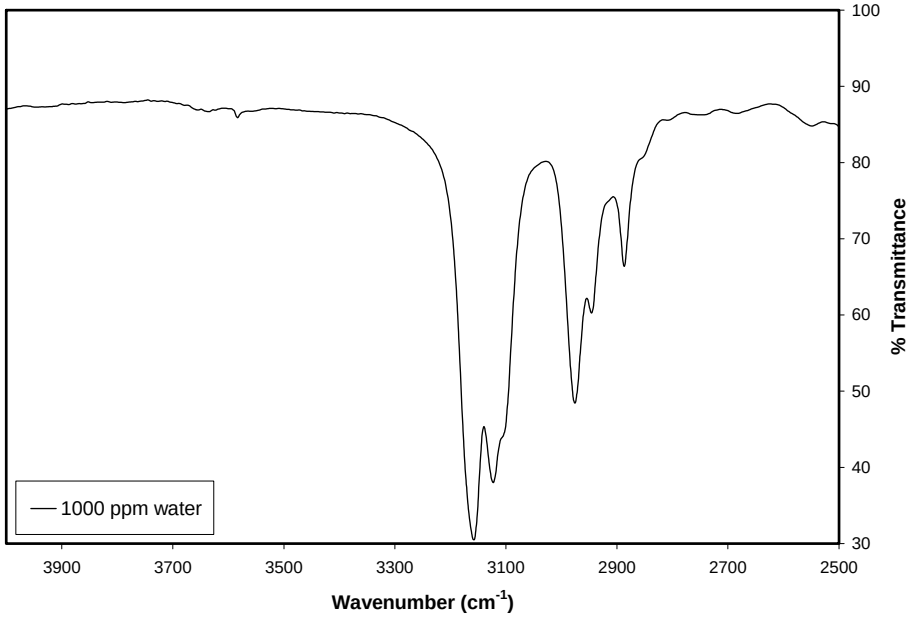

Figure 57. The IR spectra of PMIBeti with 1000 ppm water.

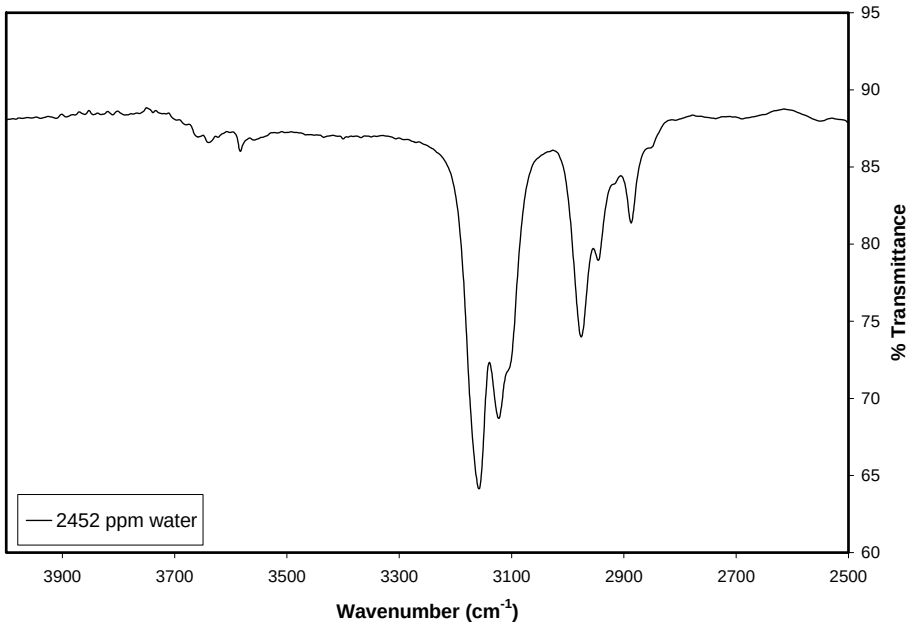

Figure 58. The IR spectra of PMIBeti with 2452 ppm water.

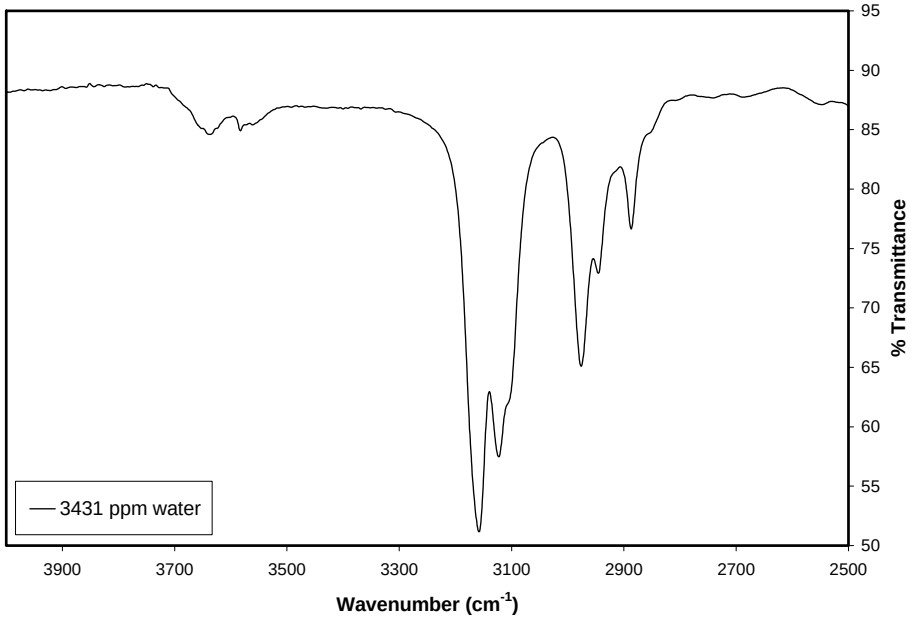

Figure 59. The IR spectra of PMIBeti with 3431 ppm water.

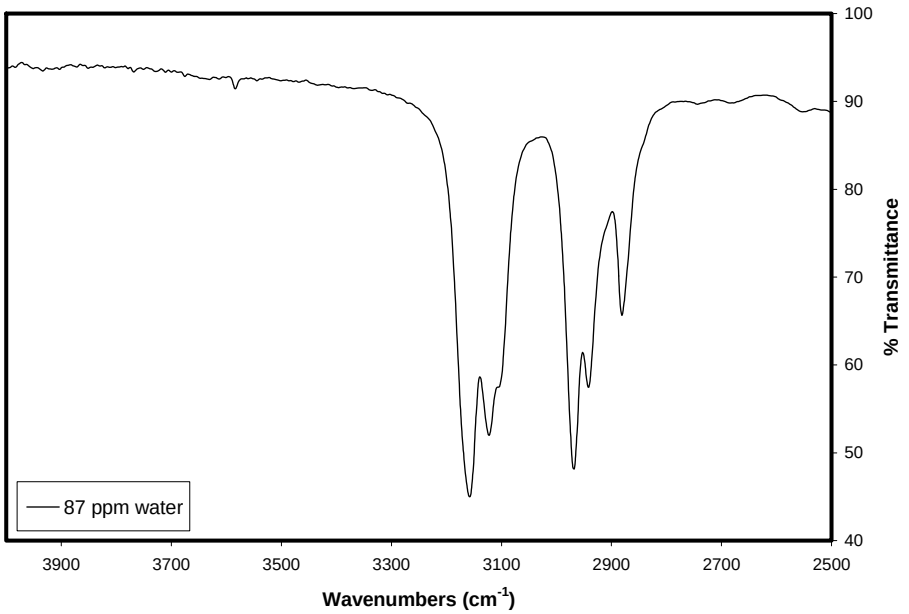

Figure 60. The IR spectra of BMIBeti with 87 ppm water.

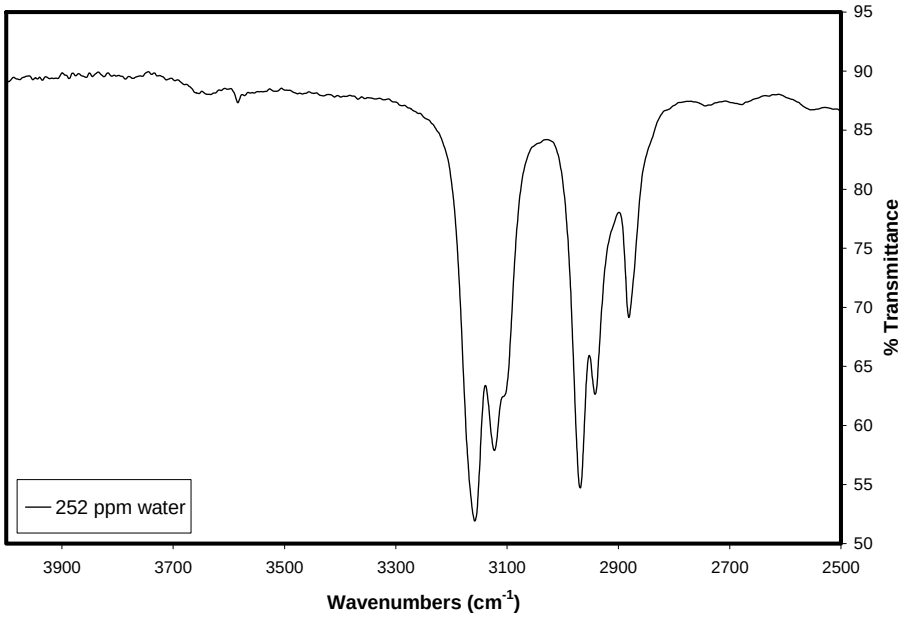

Figure 61. The IR spectra of BMIBeti with 252 ppm water.

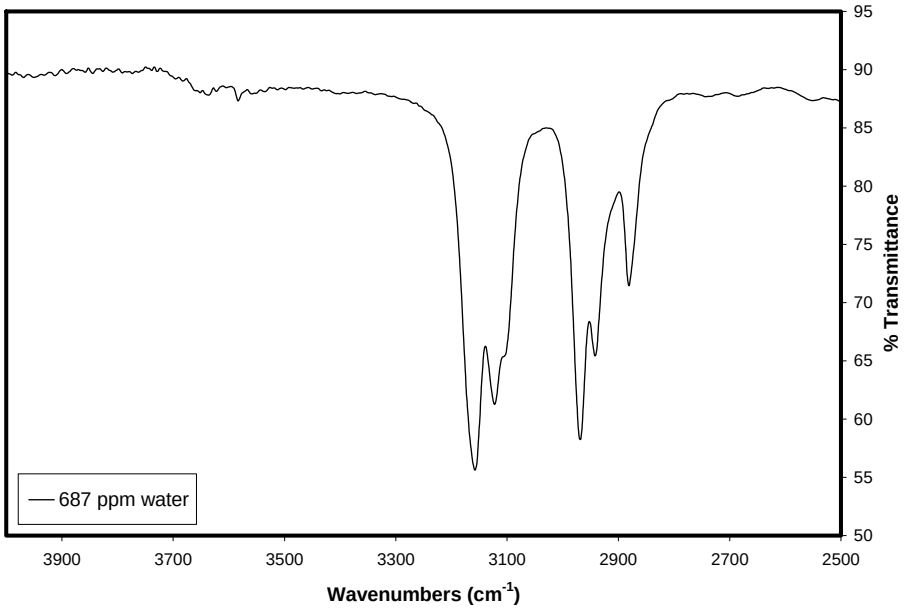

Figure 62. The IR spectra of BMIBeti with 687 ppm water.

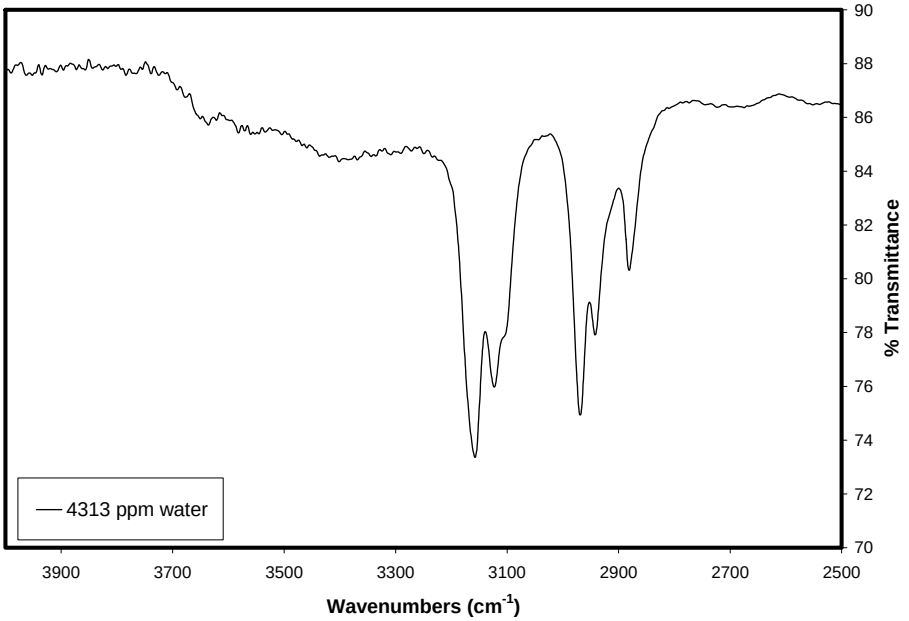

Figure 63. The IR spectra of BMIBeti with 4313 ppm water.

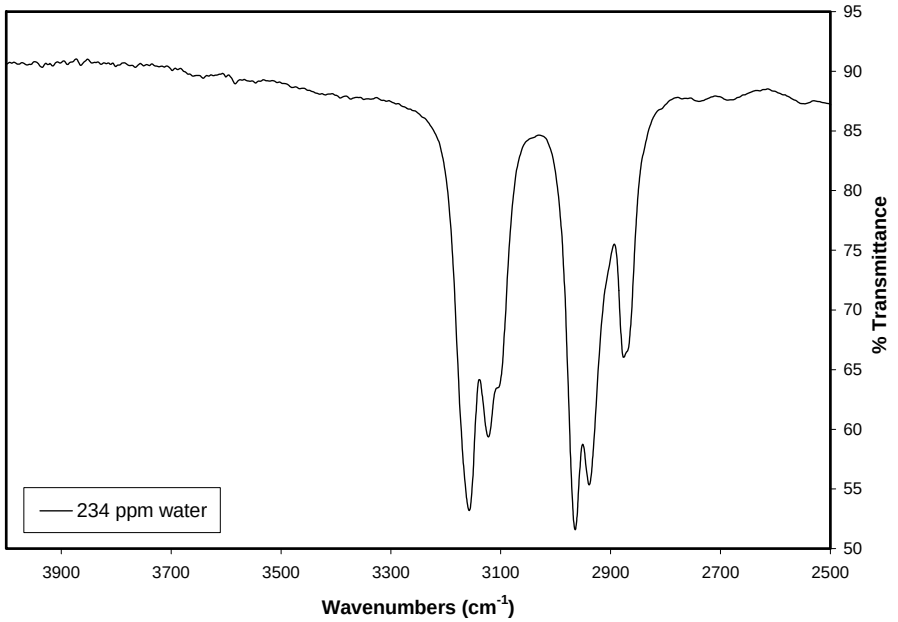

Figure 64. The IR spectra of PnMIBeti with 234 ppm water.

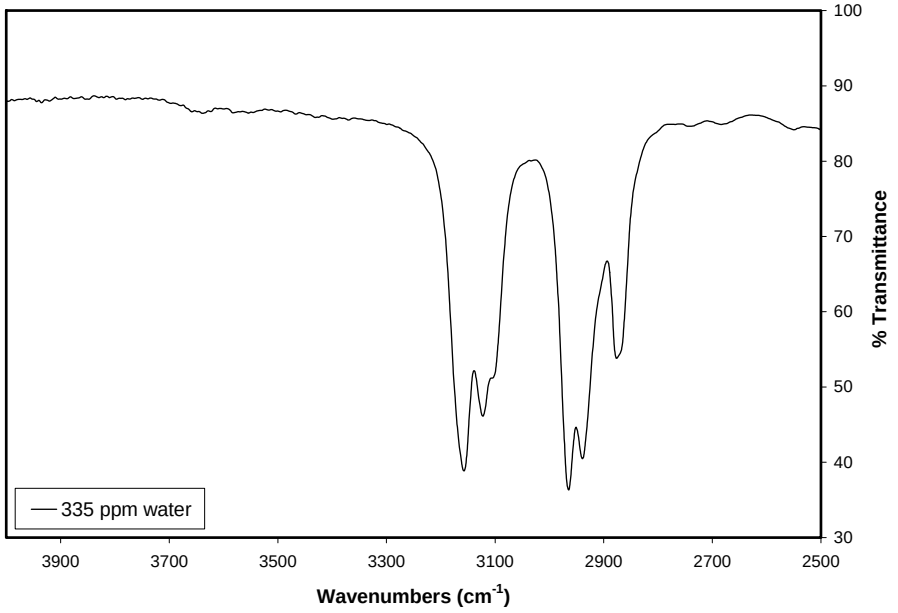

Figure 65. The IR spectra of PnMIBeti with 335 ppm water.

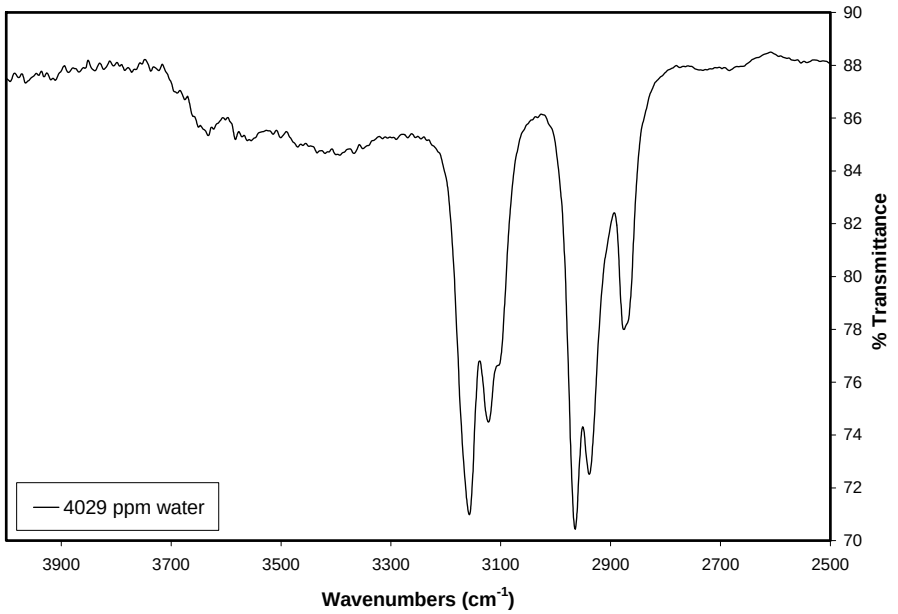

Figure 66. The IR spectra of PnMIBeti with 4029 ppm water.

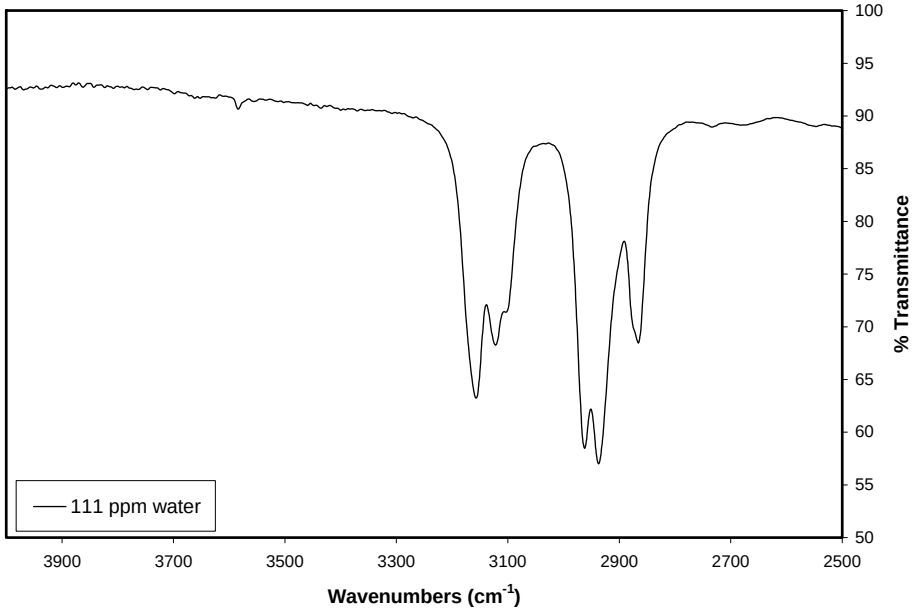

Figure 67. The IR spectra of HMIBeti with 111 ppm water.

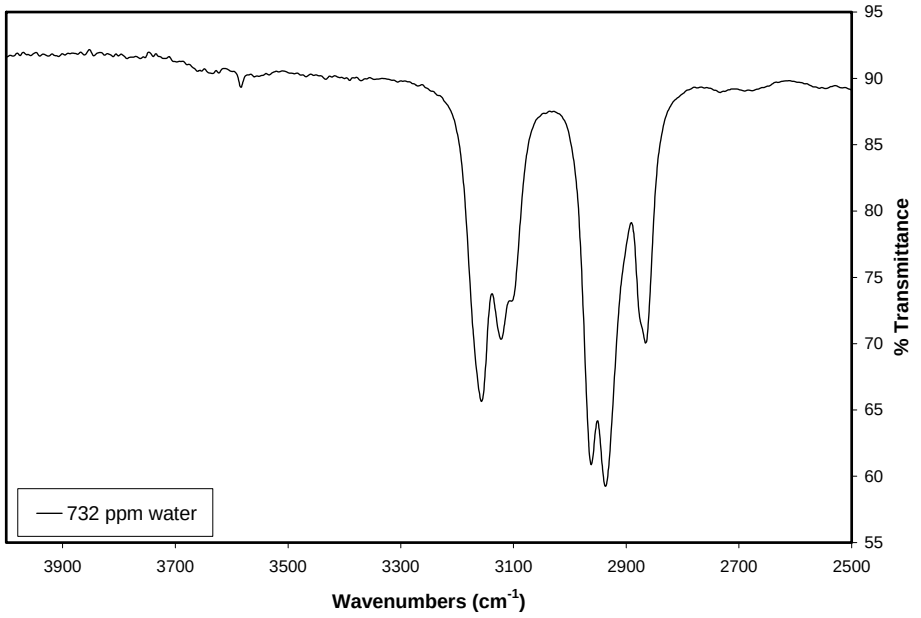

Figure 68. The IR spectra of HMIBeti with 732 ppm water.

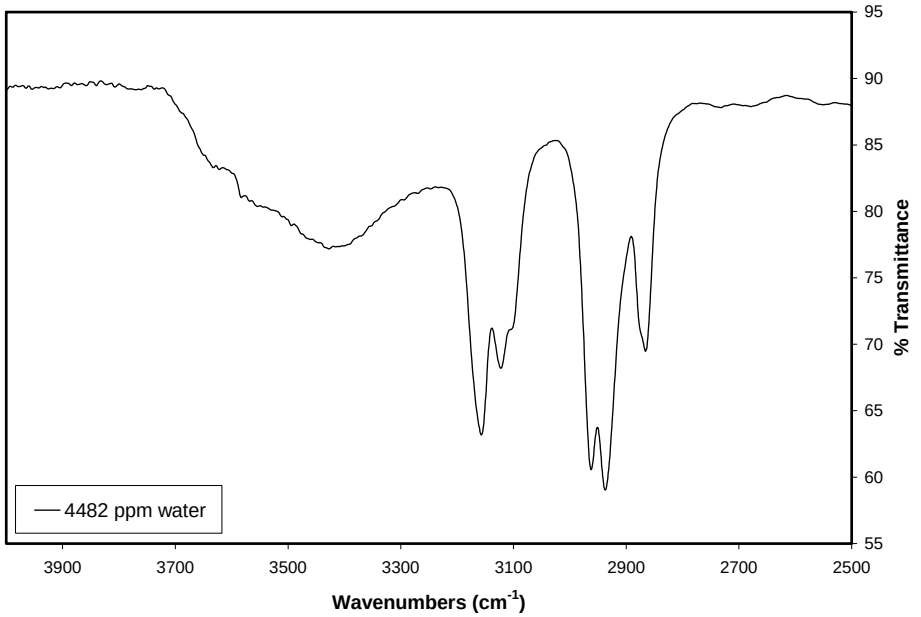

Figure 69. The IR spectra of HMIBeti with 4482 ppm water.

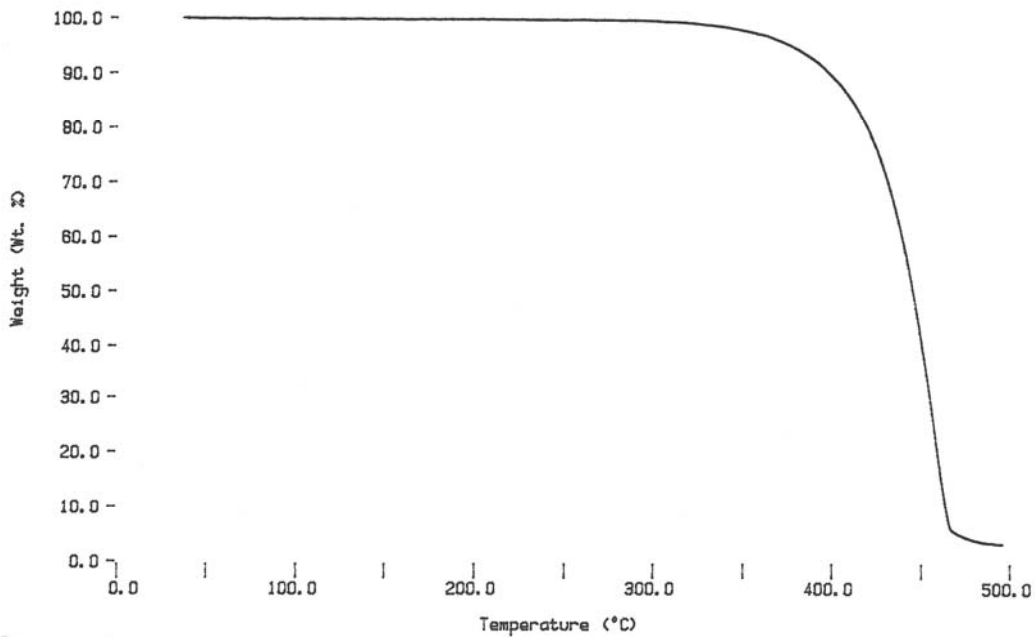

Figure 70. The thermal decomposition curve of EMIBeti.

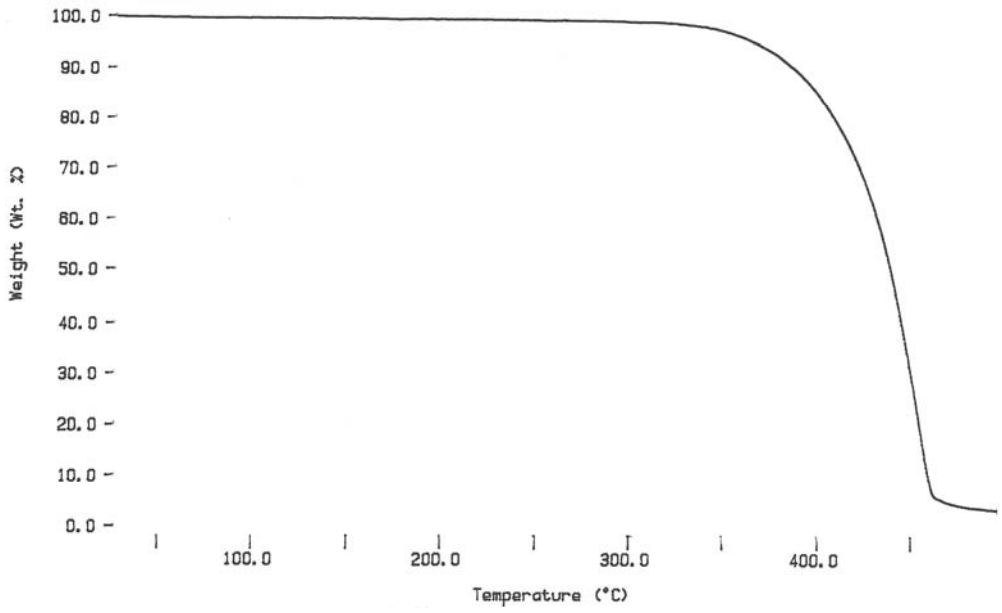

Figure 71. The thermal decomposition curve of PMIBeti.

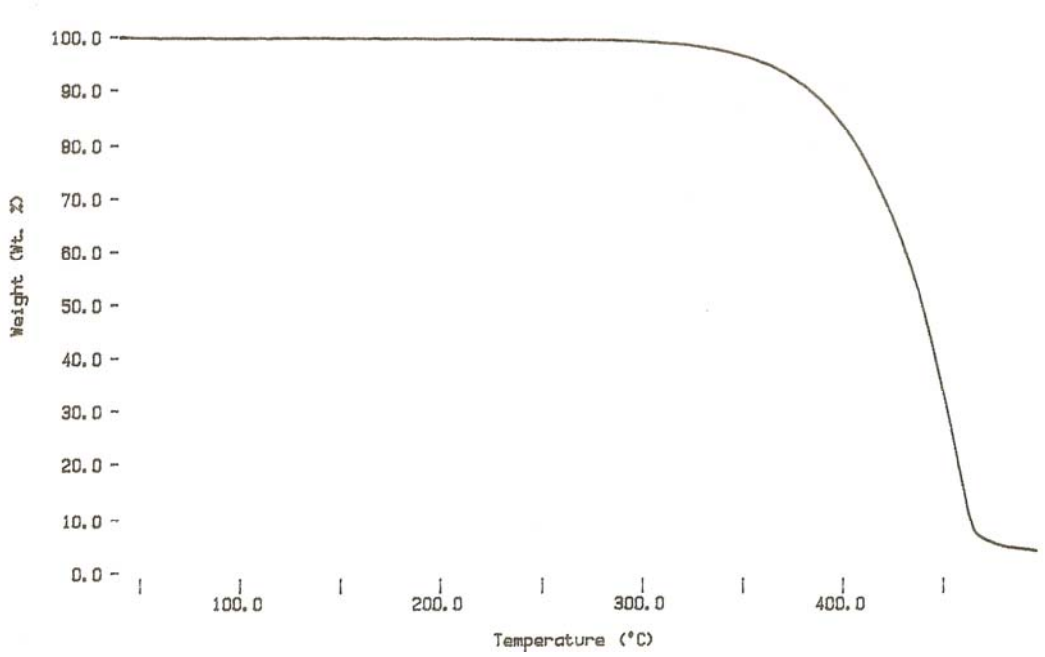

Figure 72. The thermal decomposition curve of BMIBeti.

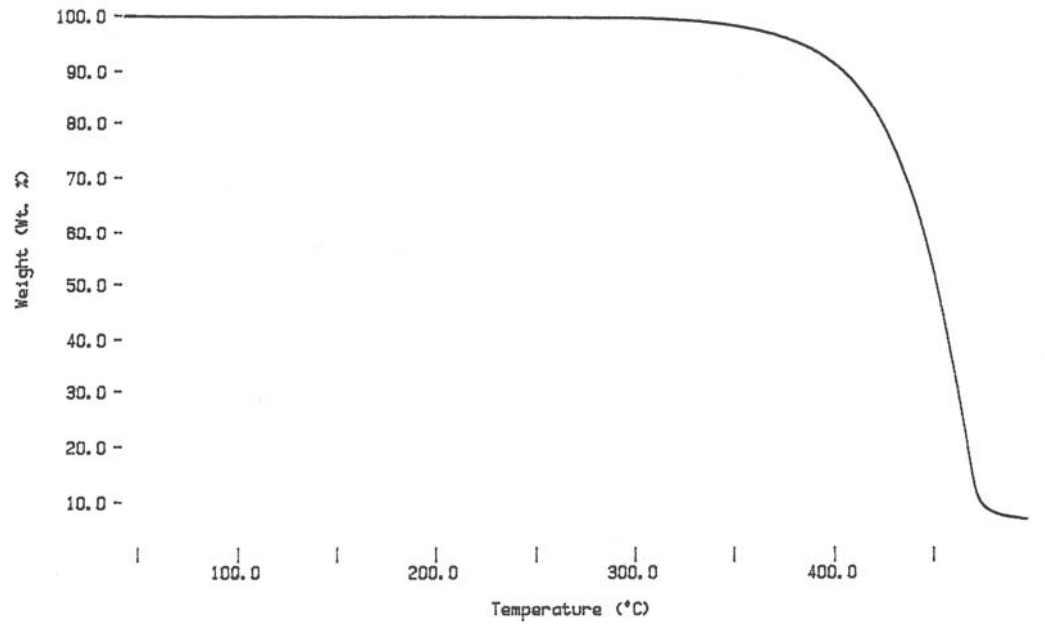

Figure 73. The thermal decomposition curve of PnMIBeti.

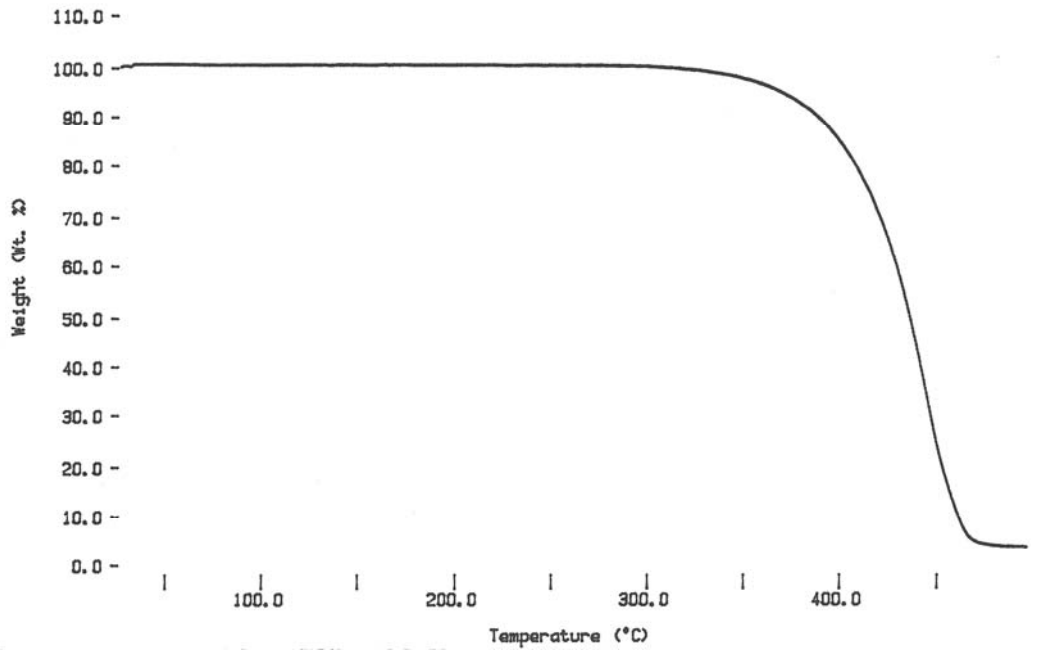

Figure 74. The thermal decomposition curve of HMIBeti.